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WILEY'S

Principles and Practice

OF

AGRICULTURAL ANALYSIS

A Manual for Students, Teachers, Analysts ~~and Investigators~~

VOLUME II

FERTILIZERS AND INSECTICIDES

THIRD EDITION

PREPARED AND ISSUED UNDER THE DIRECTION OF

THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

EDITORS

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EASTON, PA.

CHEMICAL PUBLISHING COMPANY, Inc.

1931

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PREFACE TO VOLUME SECOND

In this volume an attempt has been made to treat the subject of fertilizers and fertilizing materials in the manner followed in the first volume with soils. The general principles of fertilizer manufacture and application have been presented in so far as they seemed to throw light on the rational method of examination and analysis. The standard methods of analysis in use in this and other countries, have been presented with sufficient fullness for the guidance of the skilled worker, and the information of the student. To those who make use of a book only for routine work or for preparation for an examination, this volume, as its predecessor, will be found to have little attraction. This fact, however, will not be a cause of regret to the author whose purpose has been, avowedly, to present to the busy worker and student a broad view of a great subject which each one does not have the time to search out for himself.

It is a matter of regret, however, that the contents of the volume have again exceeded all expectations. It was found impracticable to secure any greater condensation without departing from the purpose, and impairing the completeness of the work. When work is done with no prospect of financial compensation, it is gratifying to find it appreciated, and the author will be content to have this volume meet with as kindly a reception as has been accorded volume one.

HARVEY W. WILEY.

Washington, D. C.
End of July, 1895.

PREFACE TO SECOND EDITION

A great part of the material relating to the occurrence and analysis of ammonia, nitrous and nitric acid printed in the first volume of the first edition of this work has been rewritten and transferred to this volume. This rearrangement has resulted in making the first and second revised volumes of approximately the same size.

All the matter of this volume has been rewritten and brought down to date. New features of moment are those relating to the production of nitric acid for manurial purposes from cyanamid and by direct electric oxidation of the nitrogen of the air. A chapter on the analysis of insecticides has also been added.

While not intended in any way as a laboratory guide it is hoped this volume may be even more highly appreciated than in its first form by the student, the investigator and the teacher.

HARVEY W. WILEY.

November, 1908.

PREFACE TO THIRD EDITION

A preface offers an opportunity, not always afforded by the text, for the author to formulate his vision, to emphasize what he considers the need, to define his purpose, and to acknowledge the help of co-workers in the preparation of the volume. The function of a preface of a book such as *Principles and Practice of Agricultural Analysis* is to set forth briefly the origin, the scope and the aim of the work.

In the first and second editions of Volume II the purpose of a preface is fully met by the author, Dr. Wiley. In the third edition there is presented the task of explaining with brevity, the prime requisite of every good preface, the changes in material made essential by the strides of science and new authorship. The aim of the third edition is identical with that expressed in the preface to the first edition.

The several volumes of *Principles and Practice of Agricultural Analysis* are not books of methods or manuals for the laboratory technician; rather, they supplement the "Book of Methods" of the Association of Official Agricultural Chemists. They aim, as their author succinctly announced, "to place in the hands of teachers and students of agricultural analysis and of analysts generally the principles which underlie the science and art of analysis." These principles, when mastered, will enable the student or analyst to sit quietly at his desk and interpret, construe, and evaluate the data and figures yielded by his balance, his refractometer, his microscope, his polariscope, and by other instruments of precision which he employs. The writers presuppose such a familiarity with the Book of Methods as gives point to the observation in the preface to Volume II that "To those who make use of a book only for routine work or for preparation for an examination, this volume, as its predecessor, will be found to have little attraction." To the agricultural chemist who interprets facts as he finds them, however, these volumes will prove invaluable.

The present edition is not a revision in the sense that it is a rewritten and enlarged former edition; the subject matter, the arrangement and the method of presentation are new.

When Dr. Wiley proposed to deed in trust the author's right in *Principles and Practice* to the Association of Official Agricultural Chemists, as shown by the appended letter to the Secretary, there were misgivings on the part of some of the leaders of the organization regarding the advisability of accepting the generous offer. Because of the continuity so necessary in a work of this kind, there was some doubt about the ability

of the rather loosely organized body of scientific workers, bound together solely by their official position, to push to a desirable and creditable conclusion such a herculean task as it was recognized the acceptance would entail. After careful consideration of the matter by the Executive Committee of the Association, however, it was decided to accept the gift, provided Dr. Wiley would withdraw certain restrictions he had imposed and which it seemed would make impossible the work of revision. Dr. Wiley magnanimously acceded to the suggestions of the Committee, but no doubt with regrets, because he fully realized that radical changes in his material would be necessary to swing it into step with the march of progress.

After a thorough canvass of the members of the Association available for such an undertaking, the Executive Committee selected C. A. Browne and W. W. Skinner as editors, with power to act in all matters pertaining to the policies of production and to the personnel of the contributing staff. Just two conditions were named by the Committee: That, so far as possible, the contributors should be restricted to the membership of the A.O.A.C. and that the several volumes should be closely articulated with and made supplemental to the Association's Book of Methods. In harmony with these two ideas the editors constructed their outlines for Volumes II and III and selected their collaborators. Upon these modest, painstaking men fell the burden of production and responsibility for the character of the work; to them belongs in full measure the credit for the successful completion of a difficult task. The editors have been fortunate in the whole-hearted support given to them, often at the cost of great personal sacrifice and with little hope of reward other than the satisfaction which comes from the utilization of natural talents for a great service.

That the Association of Official Agricultural Chemists is an interesting body of earnest, energetic and capable public servants was made doubly impressive to the editors when they began the work of selecting collaborators in this undertaking. They are men and women of national, indeed international, reputation in their chosen fields of activity. As the reader turns the pages and notes the authorship listed at the head of each chapter he will recognize, especially if he is versed in the literature of agricultural chemistry, that here is the production of men who speak with the authority of thorough knowledge and ripe experience. To indicate just how much the revision is a product of the A.O.A.C. it may be pointed out that in Volume II four of the eight chapters were prepared under the leadership of past presidents of the Association, and in the appended list of contributors will be recognized some of the leading minds which, as-

sociated together for a community of interest, have made the A.O.A.C. an outstanding organization.

To Miss Marian E. Lapp, the Assistant Secretary of the Association, and Associate Editor of The Journal of the Association, grateful acknowledgment is due for the tireless and efficient service rendered in bringing editorial order out of a heterogeneous mass of material of varying styles and completeness. Particularly fortunate were the editors in securing the collaboration of Dr. Edward Hart, the publisher, who has been a life-long friend of Dr. Wiley. His sympathetic support and encouragement were deciding factors in undertaking the work.

To such contributors and reviewers as R. N. Brackett, H. D. Haskins, H. B. McDonnell, A. R. Merz, W. H. Ross, G. S. Fraps, F. P. Veitch, P. E. Howard, B. B. Ross, C. W. Whittaker, J. S. McHargue, C. C. McDonnell, J. J. T. Graham, C. M. Smith and E. L. Griffin, whose work speaks for itself in the following pages, the editors owe grateful acknowledgment and the students of agricultural chemistry a lasting debt.

Washington, D. C.
September 1, 1930.

W. W. SKINNER,
Secretary-Treasurer,
Association of Official Agricultural Chemists.

PRESENTATION OF COPYRIGHT

Doctor W. W. Skinner,
Secretary-Treasurer,
Association of Official Agricultural Chemists,
Washington, D. C.

My dear Doctor Skinner :

My inability to prepare a third revision of Volumes II and III of Principles and Practice of Agricultural Analysis after Volume I of this series had been prepared and published was apparent. Failing eyesight and the fact that I had not been able to maintain that intimate contact with the progress of agricultural chemistry necessary for such a task were contributing factors in the decision to intrust this important work to others.

Owing to my close relationship with the Association of Official Agricultural Chemists, it was natural that I should wish to have this organization continue the work, and so it was with great satisfaction that I learned that my offer to present the copyright of the second and third volumes of the third revision and of all subsequent revisions had been accepted.

As evidence of my interest in this association and its aims and objects I may state that I was present at the first meeting that was held after its organization under the present name at Philadelphia, September 8 and 9, 1884, and that I have attended every meeting held since that time. I served as President of the Association in 1886, and as Secretary from 1890 until my resignation from the Bureau of Chemistry in 1912. Then I was elected Honorary President for life, and it has been my pleasure to address the members at each meeting held since that time.

I am greatly pleased to learn from you that the manuscript for the third revision of Volume II is completed and about ready for the printer, and that about three-fourths of the material for Volume III has been received by you and is being edited.

To those members of the association who have so ably contributed toward the success of the undertaking, and to Doctor C. A. Browne and to you who have been entrusted by the Executive Committee of the Association with the heavy responsibility for the planning and execution of the third revision, I wish to express my very grateful appreciation.

Sincerely,

HARVEY W. WILEY.

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PART I

FERTILIZERS

CHAPTER I

INTRODUCTION

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Definition of Terms.—A *fertilizer* may be broadly defined as any material, organic or inorganic, natural or artificial, that furnishes directly or indirectly to plants one or more of the elements necessary for normal growth.

A *direct fertilizer* is any material, organic or inorganic, natural or artificial, that either immediately through solution or after undergoing fermentation, ammonification, nitrification, weathering and other chemical changes in the soil, furnishes one or more of the elements necessary for normal plant growth.

The term *indirect fertilizer* is applied to materials, organic or inorganic, that improve the mechanical condition of the soil, neutralize acidity or assist in the liberation of plant food from various materials; they may also furnish plant food.

A *commercial fertilizer* is any material valued for its content of nitrogen and/or phosphoric acid, and/or potash, though most state fertilizer laws exempt lime, limestone and marls, and also manure when unmixed with other materials. Some state laws, however, require manures to be included under the regulatory act, exempting only the excrements and litter from domestic animals in its natural state. Some state laws set a minimum limit to the quantity of nitrogen, phosphoric acid or potash that must be present in order to classify the material as a commercial fertilizer. For example, in one of the states that produce large quantities of fertilizers, a material, substance, or mixture that is claimed to contain more than one per cent of nitrogen, or of phosphoric acid, or of potash is classed as a commercial fertilizer, provided that lime, limestone, marl, unground bone, stock-pen manure and barnyard manure shall be exempt in case the excrement or manure has not been dried, manipulated or otherwise treated, or is not claimed to have a value of more than \$4.00 per ton.

Plant food consists of all the elements that are assimilated by plants and that are necessary to normal growth. Recent investigations have shown that these elements are not restricted to fourteen: nitrogen, phosphorus, potassium, calcium, magnesium, iron, oxygen, hydrogen, carbon,

sulfur (sodium, chlorine, silicon, fluorine), as was believed for many years. To these fourteen must be added manganese, boron, copper, nickel, cobalt, zinc, and no doubt others, although the quantities of the less common elements required by plants are extremely small, only a few parts per million.

The term *manure* is often used synonymously with fertilizer, especially in England and other English speaking countries; in this country it is usually applied only to the excrement of cattle and other domestic animals, with or without the usual amount of litter or bedding used in the care of the animals: The term *guano* is applied to the accumulated excrement and remains of wild birds, as Peruvian guano, etc.

In harmony with the common practice in this country, however, the words *fertilizer* and *manure* will be used in this volume as defined.

Occurrence of Fertilizers in Nature.—In the succession of geological epochs that have marked the natural history of the earth there have been brought together in deposits of greater or less magnitude the stores of plant food unused by growing crops or which may once have been part of vegetable and animal organisms.

A full description of the extent and origin of these deposits may be obtained from works on economic geology. A brief description of them is given in this volume in connection with the fertilizing materials which they furnish. These deposits are the chief sources of the mineral fertilizers which are offered to the farmers to-day and to which the agricultural analyst devotes much of his time and labor. The methods of determining the chemical composition and agricultural value of these deposits, as practiced by the leading chemists of this country and Europe, will be fully described in the following pages.

WASTE MATTERS AS FERTILIZER MATERIAL

Natural Fertilizer Products of the Farm.—The most important of these are the excrements of domestic animals, waste residues, straw, grasses, stover, and leaves from the wood lot and forest. Wood ashes are valued especially for their potash and lime content.

Industrial Wastes.—The industrial waste materials are also important. They comprise the debris from such sources as factories and abattoirs, which is prepared for use and sold as commercial fertilizer. Among these waste materials may be mentioned bones, horns, hoofs, hair, meat scrap, blood, fish scrap, whale meat, oil cakes, ashes, sewage, garbage, offal of

all kinds, leather scraps, distillery waste, basic slag, tobacco stems and stalks, and organic debris in general.

In the last few years, however, the tankages prepared from packing house waste, fish scrap and oil cakes, with the exception of castor pomace, have been so extensively used as animal feeds that very little of such materials has been available for fertilizer. It is fortunate, therefore, that such inert materials as leather scrap, hair, feathers, and garbage can be so treated as to make them sources of soluble and available plant food, especially nitrogen.

These and other more recently found sources of nitrogen, notably synthetic nitrogen products, will be considered in their appropriate sections. Among these products are nitrate of soda, nitrate of potash, nitrate of lime, nitrate of ammonia, sulfate of ammonia, phosphate of ammonia, calcium cyanamide, urea, calurea, and leunasalpeter. Sources of phosphoric acid and potash showing high analysis such as double and treble superphosphate and kemfert, the latter a muriate of potash from the Searles Lake deposit, are also utilized. Finally, there are other high analysis products, both imported and of domestic manufacture, furnishing nitrogen, phosphoric acid and potash, such as nitrophoska and ammosphos-ko.

Trade Values of Fertilizing Ingredients in Raw Materials and Chemicals.—In some states it is customary for the fertilizer control officials to procure and publish the trade values of ingredients in the raw materials and chemicals used in compounding mixed fertilizers, and in other states this is a requirement of the fertilizer law. These trade or commercial values are usually secured from quotations given during the fall and winter seasons, and cover a period of from three to six months, as the case may be. They are usually based on the average cash prices at local centers of distribution for chemicals and raw products for the period designated, and in the New England section the usual custom is to add 20 per cent to the published quotations to cover overhead costs.

The method of calculating these trade values may be illustrated as follows: The average cash price per ton at the ports, of a raw material, say sulfate of ammonia, is divided by the percentage of nitrogen guaranteed and thus is obtained the unit value. As the unit value is the price of 20 pounds, one per cent of a ton (2000 lbs.), this value divided by 20 gives the price per pound of nitrogen in sulfate of ammonia. The following values thus obtained in one of the seaboard states in 1928 are given as an example.

	Per unit	Per lb.
N — in sulfate of ammonia	\$2.60	\$0.130
N — in nitrate of soda	3.34	0.167
N — in blood	6.32	0.316
N — in tankage	6.32	0.316
N — in ground fish	6.68	0.334
N — in cottonseed meal	6.68	0.334
Available phosphoric acid	0.80	0.040
K ₂ O — in kainit	1.05	0.053
K ₂ O — in manure salts	0.80	0.04
K ₂ O — in muriate	0.80	0.04
K ₂ O — in sulfate	1.05	0.053

From these values were taken the following figures for the ingredients in mixed fertilizers:

	Per unit	Per lb.
N	\$5.00	\$0.25
P ₂ O ₅	0.80	0.04
K ₂ O soluble in water	0.90	0.045

The following example will illustrate the use made of these values in calculating the relative commercial values per ton in mixed goods:

	N	P ₂ O ₅	K ₂ O
Guaranteed percentage	5.00	8.00	4.00
Found	5.10	8.25	4.10
5 × \$5.00 =	\$25.00		
8 × 0.80 =	6.40		
4 × 0.90 =	3.60		
	\$35.00 R.C.V. per ton guaranteed		
5.10 × \$5.00 =	\$25.50		
8.25 × 0.80 =	6.60		
4.10 × 0.90 =	3.69		
	\$35.79 R.C.V. per ton found on analysis		

These money values per ton simply represent the average cost of raw materials of good quality at the ports, at ton rates, for the period during which the trade values were obtained. They do not represent the cost per ton of the mixed fertilizer to the purchaser, because no account has been taken of costs of manufacture, freight from the ports or of any other expenses incident to the manufacture and handling of mixed fertilizers. The trade values have nothing to do with the agricultural value of the material. "The valuations of mixed fertilizers, obtained by the use of this schedule, are entirely commercial; they are not intended to indicate even a possible agricultural value."¹

¹ Vorhees' Fertilizers, 1898, 158.

Expression of Results of Fertilizer Analyses.—It has long been the custom of chemists to express the results of the analysis of minerals, and of inorganic materials generally, as oxides of the elements determined, except in the case of halides. For example, in reporting on fertilizing materials and mixed fertilizers the phosphorus is reported as phosphorus pentoxide (P_2O_5), and, in accordance with a custom prevailing in the time of Lavoisier and Berzelius, it is called phosphoric acid. In like manner potassium is reported as potassium oxide (K_2O), and called potash, though this name is also frequently applied to the hydroxide and to the carbonate, often with the added designations of “caustic” for the former and “mild” for the latter. For many years it was the custom to report the nitrogen as ammonia (NH_3), and materials were bought and sold on the ammonia basis. The rule quite generally followed now, however, is to report the nitrogen as such, since it does not usually occur in the ammoniacal form in the material sold as sources of nitrogen. Practically all states have now adopted the elemental form of reporting nitrogen.

Some chemists also advocate reporting the phosphorus and potassium as elements, and this, no doubt, is more scientific. Others, apparently still more scientific, have suggested that the ions PO_4 , K , and NH_4 or NO_3 be used in reporting results of analysis.

While both the elemental and the ionic systems of reporting results of fertilizer analyses are more scientific than the common system, it must be kept in mind that the results are reported mainly for the benefit of those who are not chemists. The common system has been established by long usage and has come to have a real and definite meaning to the manufacturers, dealers, and purchasers of fertilizers. Even the change from ammonia to nitrogen in the common system will have to be a slow one, so firmly fixed is the term ammonia in certain sections of this country. Certainly, then, a change from the common system to the elemental or the ionic, while it might have the advantage of scientific accuracy, would be extremely difficult and would unquestionably lead to confusion for a long time. Especially would this be true of the ionic system.

In considering the different forms of nitrogen, in mixed fertilizers, especially, it is customary to report nitrate nitrogen, ammoniacal nitrogen, and organic nitrogen. Until recently the ammonia equivalent of the nitrogen in its various forms has been used in some states.

CHAPTER II

SAMPLING

By H. B. McDONNELL, *M.S., M.D., Professor of Agricultural Chemistry, University of Maryland and Formerly State Chemist of Maryland*

A sample should, under average conditions, constitute a small portion of any given product taken in such a way as to be fairly representative of the original tonnage present. It should be so prepared and preserved as to prevent or reduce to the minimum either contamination or changes in composition.

All materials to be analyzed are naturally divided into three states, namely, gaseous, liquid and solid.

Sampling a Gas.—The gaseous contents of the vessel, room or other container should be thoroughly mixed in order to have any given portion represent the whole mixture. This is especially important if the components have different specific gravities and have not had time to become thoroughly mixed by diffusion. An ordinary electric fan placed in a room will so thoroughly mix its gaseous contents that a representative sample may be drawn in a short time.

To keep a sample of gas free from contamination by other gases during sampling, it may be aspirated into a vessel filled with a liquid in which the gas is not soluble. For most gases mercury is theoretically the best liquid for this purpose, but its great weight and cost practically prohibit its use. As a rule water will be found entirely satisfactory for the aspirating material, especially if the receiving vessel is sufficiently large. The quantity of gas that will be absorbed may be disregarded except when the gases are soluble in water, for example, ammonia, sulfur dioxide, etc. If the constituent sought is of sufficient concentration gases may be sampled directly into eudiometers or other vessels in which the analytical processes are to be carried out.

A sample of gas may also be secured by pumping gas from any room or confined space into a flattened dry rubber bag. To expel the last traces of air the bag may be filled at least partially with gas, the contents expressed, and the bag then refilled.

If the gas to be determined is a minor constituent of air the procedures of sampling and analysis may be combined by aspirating the air through an absorption cylinder after passing it through an ordinary gas meter fitted with a special unit-reading dial. If the gas is of a corrosive nature,

as chlorine or nitrogen peroxide, it should be passed through the absorption vessel first. In such cases the relative volume of the gas absorbed is so small that it may be neglected in the calculation. A manometer may be attached next to the meter to give the correction for reduced pressure.

When electric current is available, a small aspirating pump driven by an electric motor answers admirably for sampling. Calibrated bottles or drums of water of suitable sizes may also be used as aspirators.

The agricultural chemist may be called upon to sample gases evolved from mixed fertilizers in storage or transportation and from manure in stables or in storage, or to study the effect of smelter, or other fumes, on vegetation. In all these cases the study of the nature of the case, the experience of the analyst and the character of the analysis will determine the methods which are best adapted to the purpose.

Sampling a Liquid.—Liquids are sampled in the same general way as are gases. They should always be thoroughly mixed in order to obtain a sample that is uniform and representative in character. The mixing may be accomplished either by mechanical means, as usually practiced, or by blowing pure air through the liquid if this will cause no change by oxidation, evaporation, or expulsion of gas. The mechanical method, that is making use of paddles or other stirrers or simply agitating the container, however, is to be preferred when it can be practiced.

Sampling a Solid.—The general principles that underlie and regulate the sampling of solid materials are more varied than those for gases and liquids on account of the greater variety of conditions encountered. In order to obviate the consideration of changes in moisture content incident to the preparation and analysis of a moist sample, it is usually advisable to make a moisture determination on the original material, after which the product is partially dried at a low temperature. The partially dried product is then prepared and analyzed, the analysis including another moisture test on the dried product. The analytical results are then calculated to the original moisture basis. The sampling of each specific crude, coarse material constitutes an individual and most difficult problem. A brief discussion of the sampling of a few of these products follows:

Coarse Phosphate Rock, Bones, Tankage, Lime Stone, etc.—In sampling such products approximately equal portions may be secured from each full conveyor or bucket or from every ton by means of a shovel or scoop. If there are several thousand tons in the lot, the sample itself may weigh a ton or more. The heavy crushers and grinders of the factory are usually employed for the coarse grinding of the sample, which should be done

under the supervision of the sampler, who can then draw a suitable sub-sample from the ground material by means of a trier or other appropriate device.

Meat and Fish Scrap.—With substances that are tough and difficult to reduce, such as meat and fish scrap, portions should be selected that will furnish a fair representation of the product. The material selected should be passed through a sausage mill, and the whole quantity should be thoroughly mixed and quartered. This process should be repeated until the size of sample desired has been secured.

Deliquescent or Pasty Materials.—Many products that cannot be ground because they absorb water readily or are pasty may be subdivided by quartering until a sample of the proper size is obtained. Such of these materials as are soluble in water may, after weighing, be put in solution, the whole sample being used for this purpose. Having been brought to a known volume, an aliquot portion of the thoroughly mixed solution may be taken for analysis. Other solvents may be used for other materials, and thus the same principle is utilized to secure analytical results.

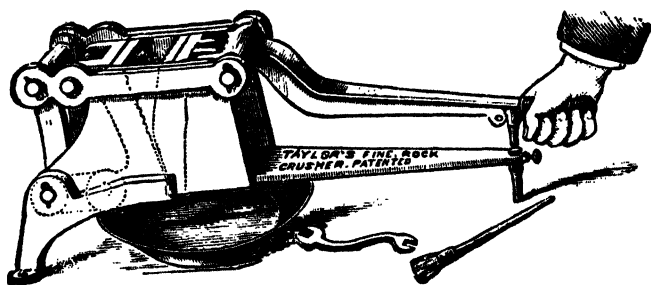


Fig. 1.—Taylor Crusher.

Liquids with Solids in Suspension.—In handling products of this nature, it is necessary to mix them thoroughly and to withdraw the desired portion as rapidly as possible, in order that the sample may contain its proportional part of the solid matter.

Garbage, Street Sweepings, Barnyard Manure, Etc.—These products may usually be conveniently sampled at the time that they are being loaded or unloaded by securing a shovelful from each full conveyor. When a sufficient quantity of the representative material has thus been secured, it should be thoroughly mixed, the larger pieces being reduced by cutting. The mixed product should then be quartered down until a sub-sample of sufficient size has been secured.



Fig. 2.—Simplex Crusher.

Minerals Containing Fertilizing Materials.—When it is possible, samples of minerals should be accompanied by a description of the mines

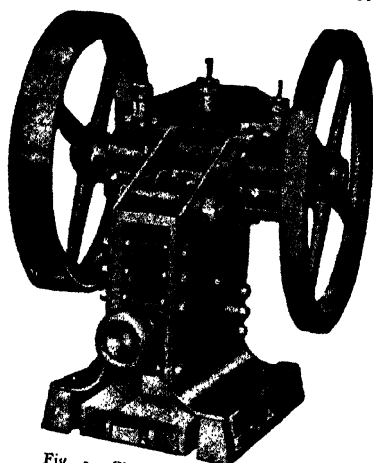


Fig. 3.—Chipmunk Crusher.

where they were procured and by a statement of the geological conditions in which the deposits were made. The sample, which should be sufficiently large to be thoroughly representative, should be put through a crusher (Figs. 1, 2 and 3) to break the mineral into small fragments. The fragments can then be reduced to a powder by grinding in a large iron mortar (Fig. 4), by means of an iron plate and crusher (Fig. 5), or in a hand or



Fig. 4.—Iron Mortar.

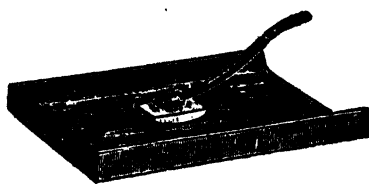


Fig. 5.—Iron Plate and Crusher.

power mill (Fig. 6). When only a small quantity of the mineral is at hand, an iron mortar and pestle will answer very well for both crushing and grinding. If the final sample is to be dissolved in an acid for soluble

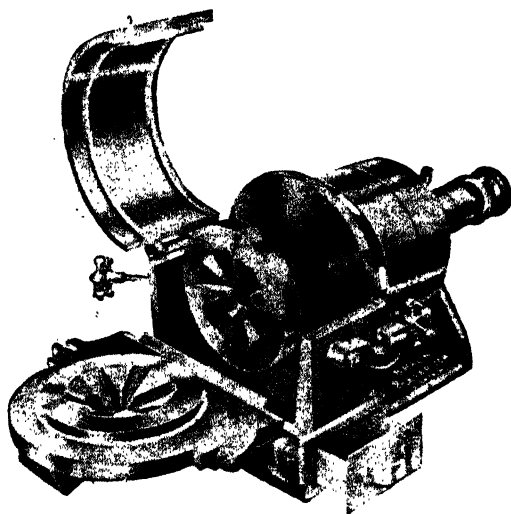


Fig. 6.—Braun Pulverizer.

materials only, it is made sufficiently fine to pass a sieve having circular openings $\frac{1}{2}$ mm. in diameter. The powdered mineral should be stirred with a magnet to remove all iron particles that may have been incorporated with it by abrasion of the implements employed in its preparation. If the original product contained magnetic material, this stirring treatment should be omitted. If a mineral analysis of the sample is to be made, it should be reduced to an impalpable powder in an agate mortar.

Commercial Fertilizers; Feeds; and Dry, Powdery Materials in Bags, Barrels, or in Bulk.—For the sampling of products of this character, several sampling tubes have been devised, all built on more or less the same principles and each one having its advocates. Practical tests of several types of open and closed samplers¹ have shown that there is little difference between the different types in regard to the reliability of the samples obtained and that the matter is largely one of convenience and the preference of the official in charge.

Sampling Tubes.—One of the simplest samplers (Fig. 7) consists of a brass tube about 30 inches long and 1 to 1½ inch in external diameter, with a wall at least 1/16th inch in thickness. A slot ½ inch wide is cut length-

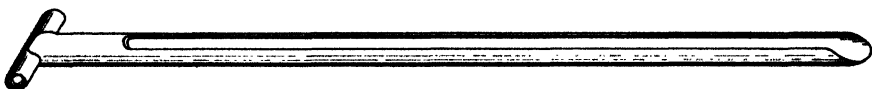


Fig. 7.—Simple Slotted Sampler.

wise in the tube to about 3 inches from the handle, which is a piece of brass tubing about 4 inches long and ¾ inch in diameter, fitted and brazed on. The cut edges of the slot should be parallel to each other (not in line) so as to make the outer edges of the slot somewhat sharp. The point of the sampler is cut off at an angle of about 45° and sharpened. When sampling, the bags should be horizontal or nearly so; the sampler should be inserted with the slot down so that it will fill as it enters with little disturbance of the contents of the bag, then turned with the slot up and withdrawn. If the sample does not flow out of the sampler it is easily removed with the end of a brush or spoon handle, and the inside of the sampler is easily cleaned with a small, flat brush. It is generally carried in a canvas and leather case, similar to a gun case.

The handle of the sampler can be made by bending the end of the tube in a semicircle, like the handle of a cane or umbrella, and by using a telescopic case or scabbard made of tin or thin metal, enameled, with ferrule at end, the whole looks like a walking stick.

Aluminum tubing may be used for the sampler but it is not so rigid as brass tubing. Steel tubing is stronger than brass but is apt to rust, especially when used for sampling fertilizers.

¹ *J. Assoc. Official Agr. Chem.*, 4, 594, 597 (1921).

The Kellogg sampler, or "Horn" (Fig. 8) is similar to the sampler shown in Fig. 7, except that it is made in two sections to facilitate carrying. Each section has a slot that does not quite reach to its respective ends, and the point is protected by a removable cap. Only the



FIG. 8.—Kellogg Sampler, or "Horn"

left-hand edge is made sharp and for this reason when used the sampler should be rotated to the right. The outside diameter of the tube is $1\frac{3}{16}$ inches.

The Indiana sampler (Fig. 9) consists of a brass tube within a tube, and it has openings $\frac{1}{2}$ inch wide, which match each other. A turn of the handle revolves the inner tube, and an indicator on the handle shows whether it is open or closed. The total length is 36 inches, and the diameter of the outer tube is 1 inch. The sampler is inserted closed,



Fig. 9.—Indiana Sampler.

then opened; the bag is shaken and the sampler is closed and withdrawn.

One of the tubes that has been found effective in securing representative samples is made of stiff brass pipe about $1\frac{1}{8}$ inches in diameter and 24-30 inches long, with a handle, or if preferred a cap, of the same material attached at the upper end. A slot about $\frac{1}{4}$ inch wide extends from a point about 3 inches from the handle to about $1\frac{1}{2}$ inches from the lower opening; it is provided with a cutting edge so that when the tube is inserted in any container and rotated to the right, it will fill the entire length even though the product which is being sampled may be more or less moist. The lower part of the tube is cut off at an angle of about 35° and it has a cutting edge. To provide for cleaning the tube, a large sized test-tube brush may be soldered to a piece of wire of sufficient diameter to preserve the proper rigidity when in use.

Illustrating the Use of the Sampling Tube.—In sampling materials contained in sacks, the trier is inserted lengthwise of the container,

which should be tipped to an angle; in some cases it should be in a horizontal position, particularly if the substance which is being sampled is in a dry, powdery form. In the case of hand-sewed sacks, the trier can usually be passed between the stitches. Most sacks, however, are machine sewed, thus necessitating the cutting of a few stitches, which should always be reseeded after the sampling is completed. The sack itself should never be perforated.

Proportion of Sacks or Containers to be Sampled.—In many of the states the method of securing samples of commercial fertilizers and cattle feeds is definitely prescribed by law, although many of the details are left to the control official in charge. The methods of the A. O. A. C. give the following directions:

Each official sample sent to the laboratory shall consist of at least 1 pound of the material taken in the following manner; Use a sampler that removes a core from the top to the bottom of the bag. Take cores from not less than 10 per cent of the bags present, unless this necessitates taking cores from more than 20 bags, in which case take a core from 1 bag for each additional ton represented. If there are less than 100 bags, sample not less than 10 bags; if less than 10 bags, sample all bags. Thoroughly mix the portions taken on a clean oil cloth or paper, reduce by quartering to the quantity of sample required, and place in an air-tight container.

Sampling agents should always be provided with proper blank forms and labels for the purpose of keeping a full record of each sample.

Mechanical Separation of Ingredients in Transit.—As a rule there will not be much segregation of the ingredients after a mixture has been made. There are exceptions, however, largely confined to fine, heavy ingredients and granular products of a somewhat coarse nature. Memorandum notes should always be made in such cases and should accompany the sample.

Preparation of Samples.—A detailed description of the processes to be followed in the preparation of such a variety of materials as usually comes to the attention of the average agricultural chemists is practically impossible. The good judgment of the one in charge must point the way in securing reasonably satisfactory results. Patience and ingenuity will lead to the solution of the most intricate problems that may arise.

Sub-divisions of Samples.—The extent to which a sample should be subdivided depends entirely upon its nature and the character of the examinations to be made. In general, it may be said that the finer the sub-division, the better the analytical results. However, unnecessary

grinding and sieving are objectionable owing to mechanical losses and the almost inevitable change in moisture content that takes place. The sample may be selected advantageously from a larger quantity of reasonably fine material by repeated quartering. Thus the final sample is kept to a small bulk. In sub-sampling materials having both fine and granular particles, particular care should be taken to see that the final sample secured is fully representative. In such cases a scoop having sides that are perpendicular to the bottom may be recommended. The use of such an instrument prevents the granular material from rolling off, as would be the case were a spatula or trowel employed in filling the bottle.

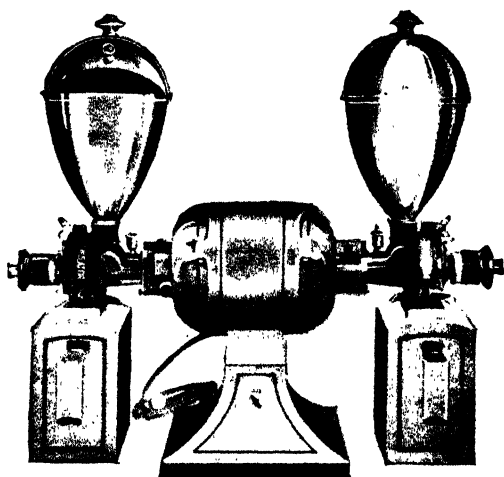


FIG. 10.—Coffee Mill.

Mills for Grinding Samples.—Several iron mortars and pestles of assorted sizes will be found to answer most requirements even in large laboratories. They are inexpensive and easily cleaned. The larger sizes may be used for crushing moderately large, hard pieces of at least 1 kg. in weight and the smaller sizes are used for the finer grinding (Fig. 4). A convenient crusher is the Taylor crusher, Fig. 1. A larger machine is the Simplex crusher, Fig. 2, and a still larger, requiring about 1 h.p., is the Chipmunk crusher, Fig. 3.

For larger laboratories one or more power-driven grinders are desirable. A commercial coffee mill, such as is used in retail stores, with two grinders attached to one electric motor, one for coarse grinding, the other for fine grinding, gives excellent results with some materials, especially organic

materials. It is possible to have the mill slightly altered at the factory so that it can be quickly and conveniently opened for cleaning after each sample is ground (Fig. 10). For grinding fibrous materials and organic matter, without grit, the Wiley mill has many advantages. It subdivides by cutting, rather than by rubbing and crushing, thus avoiding excessive heating of the sample. It also has removable screens or sieves and delivers the samples sifted (Fig. 11).

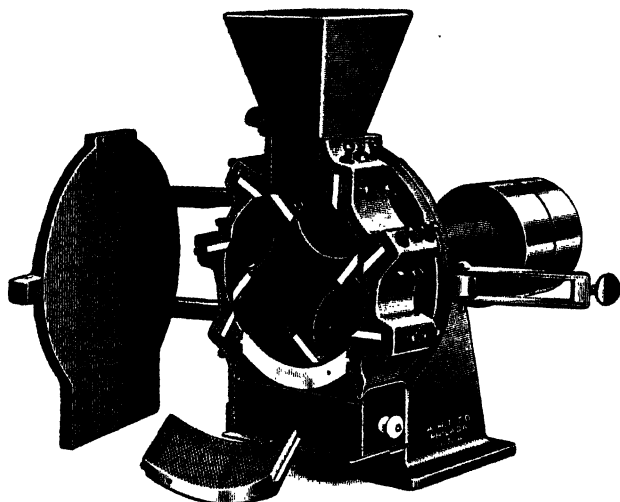


Fig. 11—Wiley Mill.

To assist in preparing samples consisting of or containing coarse litter, straw, fodder, etc., a bagasse cutter, similar to a bread slicer or meat slicer, will be found convenient (Fig. 12).

In the preparation of fertilizer samples, *Methods of Analysis, A. O. A. C.*, gives the following directions:

Pass the entire sample submitted to the chemist through a 10-mesh sieve previous to its subdivision for analysis. Reduce the gross sample by quartering to a quantity sufficient for analytical purposes. Transfer to a sieve having circular openings $\frac{1}{25}$ inch (1 mm.) in diameter and sift, breaking the lumps with a pestle. Grind the portion remaining on the sieve until all particles will pass through. Grind and sift as rapidly as possible to avoid loss or gain in moisture during the operation. Mix thoroughly and preserve in tightly stoppered bottles.

Preservation of Sample.—Samples that are reasonably dry and that are not greasy, acid or caustic may be placed in tin boxes provided with screw or friction tops, or they may be placed in paraffined paper bags which are



FIG. 12.—Bagasse Cutter.

fitted into cardboard cartons to facilitate their shipment to the laboratory. All samples should be sealed before leaving the sampling agent's hands, and as soon as they reach their destination they should be immediately transferred to suitable glass containers provided with air-tight stoppers and again sealed. Paper seals may be used to advantage at this point, but they should carry some identification marks that are not easily imitated. Samples should be kept in a dry, cool, dark room and under lock and key.

CHAPTER III

MOISTURE

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Water in Fertilizers.—Water is always present as a natural constituent of fertilizers, but the quantity varies considerably with different materials. At times it constitutes the larger portion of the product, holding in solution or suspension the solid fertilizing as well as other ingredients. Occasionally it fills partially or wholly the interstices of a fertilizer consisting of a collection of solid components and having more or less wet exposed surfaces. Usually, however, the presence of the water is not manifest, and the fertilizer has every appearance of being a dry solid aggregate.

Hygroscopic Water.—In common with most solids fertilizers possess the property, when exposed to the air, of attracting to their surfaces water vapor, which is always present in the atmosphere. This phenomenon, as a whole, is called *sorption*. When the water vapor is simply condensed and forms a film upon the surfaces of the solid it is known as *adsorbed water*. If, however, in addition to the pure adsorption, there is a solution of the vapor within the interior of the solid itself the water thus imbibed is termed *absorbed water*. There appears to be some confusion in the use of the words absorption and adsorption, and many writers use either one or the other exclusively to designate the same phenomenon. In general, the water that a substance takes up from the air is known as *hygroscopic water*. It is customary, however, to speak of those substances as being hygroscopic which, at ordinarily prevailing atmospheric humidities, attract sufficient moisture to become damp or, in the case of soluble solids, to show visible evidence of solution. This process of solution in condensed atmospheric water vapor is termed *deliquescence*.

The quantity of hygroscopic water which an insoluble substance will hold depends upon the physical and chemical nature of the material, the relative humidity of the atmosphere to which it is exposed and the temperature. In Table I are given the quantities of water which various commercial fertilizer materials were found to hold after exposure for 7 days at 20.1° C. to atmospheres of different relative humidities.¹

¹ Beaumont and Mooney, *Ind. Eng. Chem.*, **17**, 636 (1925).

TABLE I.—WATER HELD BY VARIOUS FERTILIZER MATERIALS AFTER EXPOSURE TO ATMOSPHERES OF DIFFERENT RELATIVE HUMIDITIES.

Material	Water, based on oven-dry weight		
	Relative humidities		
	Per cent 78	Per cent 87.75	Per cent 97.5
	Per cent	Per cent	Per cent
Cyanamide	6.1	13.0	21.1
Tankage	12.8	20.7	27.7
Ground fish	10.0	17.5	20.1
Bone meal	0.2	10.4	16.1
Cottonseed meal	15.7	22.9	29.6
Superphosphate	4.1	15.7	29.6
Calcined phosphate	0.4	0.5	1.5
Rock phosphate	2.8	4.2	6.7

When a soluble solid is exposed to an atmosphere having a relative humidity greater than that corresponding to the vapor pressure of the saturated solution of the solid it will continue to abstract water from the atmosphere until the resultant solution reaches a dilution where its aqueous vapor pressure equals the partial pressure of the water in the atmosphere. Table II gives the vapor pressures at 25°, 30° and 40° C. of the saturated solutions of a number of fertilizer materials and the corresponding relative atmospheric humidities.¹ Exposure to relative atmospheric humidities above these values will cause these materials to deliquesce.

Water of Combination and Constitution.—Some fertilizer products contain water of crystallization. This expression refers to the definite quantity of water which a substance includes when it crystallizes from aqueous solutions, *e. g.*, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Such solids are also called hydrates and are said to contain water of hydration. The term, water of hydration, however, has a variety of meanings. Thus it is sometimes applied to the indefinite amount of water which certain colloids contain when they separate in a gelatinous state from aqueous solutions, as well as to the water which combines with oxides to form hydroxides (acids and bases). On drying such a colloid the water passes off continuously with rise of temperature without any indication of the existence of a definite compound. This is not true, however, with hydroxides and with hydrates containing water of crystallization, in which the water appears to be an integral part of the molecule. The crystalline hydrates are frequently considered compounds in which the molecules of water are combined as such, whereas in hydroxides the water molecules lose their identity by combination with the oxygen atoms of the oxides to form hydroxyl groups. Water, how-

¹ Adams and Merz, *Ind. Eng. Chem.*, **21**, 305 (1929).

TABLE II.—RELATIVE HYGROSCOPICITIES OF FERTILIZER MATERIALS.

Material	Vapor pressure of saturated solution at—			Humidity of air in equilibrium with solution at—		
	25° C.	30° C.	40° C.	25° C.	30° C.	40° C.
	Mm. Hg.	Mm. Hg.	Mm. Hg.	Per cent	Per cent	Per cent
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	12.04	14.88	19.68	50.5	46.7	35.5
NH_4NO_3	14.94	16.93	29.11	62.7	59.4	52.5
NaNO_3	17.73	23.07	38.81	74.4	72.4	70.1
$\text{CO}(\text{NH}_2)_2$	18.06	23.09	37.66	75.8	72.5	68.0
NH_4Cl	18.12	24.61	40.81	76.0	77.2	73.7
$(\text{NH}_4)_2\text{SO}_4$	19.50	25.22	43.32	81.8	79.2	78.2
KCl	19.89	26.75	44.99	83.4	84.0	81.2
KNO_3	21.94	28.84	48.67	92.0	90.5	87.9
$\text{NH}_4\text{H}_2\text{PO}_4$	21.91	29.18	50.05	91.9	91.6	90.3
KH_2PO_4	22.76	29.60	51.46	95.4	92.9	92.9
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	22.89	29.85	52.37	96.0	93.7	94.5
K_2SO_4	23.56	30.68	53.04	98.8	90.3	95.7
						95.8

soever combined in the molecules of the substance, is called *water of combination*. That water, however, which is not supposed to exist as such, but which forms as a result of the union of hydrogen with oxygen or hydroxyl groups when a substance is decomposed by heat, is known as *water of constitution*.

Occluded Water.—Fertilizer salts may also contain *occluded water*, that is water, or rather mother liquor, which has been mechanically entrained within the crystals during the process of crystallization. This water is frequently called *water of decrepitation* since, when heated, the crystals fly to pieces explosively as a result of its vaporization.

Difficulties of Desiccation and Sources of Error.—From the preceding discussion of the states of water in fertilizers it is evident that the quantity of water which a given fertilizer contains varies with the conditions to which it has been exposed. As a consequence the composition of the fertilizer as a whole is likewise subject to changes. To compare the results of analyses which have been made directly upon samples taken at different times it is necessary, therefore, to calculate these results to a common basis of water content, or to bring the samples before analysis to a state wherein they all contain the same quantity of water. The problem is then presented of the selection of this state. Some of the water, such as water of crystallization, must be considered an essential constituent of the fertilizer and should not be interfered with. The aim should be, however, to remove all water not inherent in the fertilizer ingredients. This water, which is uncombined and usually accidentally admixed or mechanically adhering to the fertilizer, is commonly termed “moisture.” It is customary to free a material from its non-essential water by drying or desiccating at, or slightly above, the temperature of boiling water until there is no further loss of weight. The difference in weight before and after drying determines indirectly the original moisture content of the sample. When the material contains so much uncombined water as to be liquid the greater part of the water is removed by a preliminary evaporation to so-called “dryness,” and the residue is then dried to constant weight in the manner just stated. The final weight in such case is used to express directly the “total solids” or “dry matter” in the original material.

This method of determining moisture, apparently simple, is beset with many difficulties. It is sometimes impossible to remove the moisture by drying at 100° C. without liberating simultaneously all or part of the water of crystallization of certain salts. Again, water of constitution may be set free and lost. There may also be a loss of other essential consti-

tueents from the fertilizer, either directly or as a result of decomposition. Furthermore, when certain organic ingredients are present oxidation and charring may occur. The presence of organic matter sometimes results also in the formation of hard clumps or of hardened films that retain moisture mechanically enclosed or, in the case of certain liquids, of viscous masses from which the water cannot escape. These are often absorbed in asbestos, sand, etc., with previous dilution if necessary, before they are dried. Lastly, in those cases where free sulfuric or phosphoric acid is present desiccation at such a temperature is practically impossible owing to the highly hygroscopic nature of these acids in a concentrated state. Examples of such untoward factors are the loss of water of crystallization by monocalcium phosphate and gypsum, of ammonium carbonate by manure and urine, and of ammonia by diammonium phosphate and guano.

In addition to these sources of error, there is another involved in all methods wherein the material is deprived of its moisture and then weighed, because an appreciable increase of weight may take place during the process of weighing after the material has been transferred from the desiccator to the balance pan. To minimize this increase in weight, due to the sorption of moisture from the atmosphere, two watch-glasses with ground edges (one covering the other and held by a clip), stoppered glass weighing bottles, or flat-bottomed aluminum dishes with fit-over or slip-in lids are commonly used. No general method is suitable for the determination of moisture in all materials; consequently an accurate determination can only be secured in many cases by a comparison of the results of a number of methods and even then it may be doubtful which, if any, gives the true result for the material examined.

METHODS OF DETERMINING MOISTURE IN DIFFERENT PRODUCTS

Drying at Low Temperatures and Ordinary Pressures.—The moisture content of materials is frequently, and often through necessity, determined by procedures which do not subject them to temperatures above those ordinarily prevailing in the laboratory. The procedure most commonly used is to confine the substance in a closed space containing another substance that has a greater power of removing moisture from the atmosphere which surrounds them. Mention has already been made of the power of different substances of extracting water from the air. This power is greatly enhanced when the condensed water enters into chemical

combination with the substance. Compounds that exhibit this power in high degree are used as drying agents and are called *desiccants*. Desiccants may be grouped in four classes: (1) soluble compounds that form saturated solutions with very low vapor pressures; (2) compounds that unite with water to form hydroxides; (3) compounds that combine with water to give crystalline hydrates; and (4) substances that react with water in other ways. To class 1 belong sodium and potassium hydroxides; sulfuric acid may also be properly placed here although it is miscible with water in all proportions; calcium oxide and phosphorus pentoxide come under class 2; examples of class 3 are calcium chloride and magnesium perchlorate; and metallic sodium and calcium carbide¹ illustrate class 4. When the desiccating agent and the material that is to be dried are placed in the closed chamber (desiccator) moisture is withdrawn from the confined air by the former (desiccant) and given up to it by the latter. This process continues until a state of equilibrium is reached wherein all or practically all the moisture has been removed from the material under examination.

Another procedure is to deprive air of its moisture by passing it through a tube containing a desiccant and then to pass the dried air over or through the substance whose moisture is to be removed.

The following list includes, in the order of their desiccating power (activity), various substances that are used as desiccants:

- Phosphorus pentoxide.¹
- Magnesium perchlorate, anhydrous.²
- Magnesium perchlorate, trihydrate.²
- Potassium hydroxide, fused.³
- Aluminum oxide.⁴
- Sulfuric acid, anhydrous.³
- Magnesium oxide.⁴
- Sodium hydroxide, fused.³
- Calcium bromide, anhydrous.⁵
- Calcium oxide.⁴
- Calcium chloride, anhydrous, granulated.⁶
- Sulfuric acid, 95.1 per cent.⁴
- Calcium chloride, anhydrous, fused.³
- Zinc chloride, anhydrous.⁵

¹ McGee, W. J., *J. Assoc. Official Agr. Chem.*, **1**, 218 (1915); Clark, J. O., *Ibid.*, **4**, 48 (1920).

Zinc bromide, anhydrous.⁵

Copper sulfate, anhydrous.⁴

Anhydrous barium perchlorate has recently been shown to be a very satisfactory desiccant.⁷ Boric acid anhydride has also been recommended.⁸ When dehydrating agents that liberate a gas as a result of reaction with the water vapor are used, the closed chamber must have a vent for the escape of the gas. This vent should be provided with a mercury or other seal.

The choice of a drying agent is determined by a number of considerations besides its drying activity or desiccating power. Among these are its drying capacity or the weight of moisture that it can take up per unit of its own weight, its capability of being restored to its original power and capacity and the ease with which this can be done, its physical state (whether liquid or solid), its capacity for granulation, its cost, and its corrosiveness.

Calcium and magnesium oxides have very small capacity for moisture. Potassium hydroxide is less easily handled than alumina although it is more easily prepared. Alumina, in comparison with sulfuric acid, is not subject to slopping, which may cause burns or other injury, and it can be reused frequently, for though it has a comparatively low capacity it can be easily reactivated. Anhydrous magnesium perchlorate has several times the capacity of phosphorus pentoxide, does not become sticky upon handling, can be reactivated repeatedly and is a neutral drying agent.

Two forms of desiccators in general use are illustrated in Figs. 1 and 2. The Scheibler desiccator is adapted to the use of sulfuric acid as a drying agent, the shape of the lower portion being such as to limit splashing or spattering of the acid. The Frühling and Schultz desiccator, which is shown in the illustration with a porcelain desiccator plate on which are placed the vessels containing the substances to be dried, is suited to the use of solid desiccants, the large opening between the upper and lower sections facilitating the filling of the latter with the desiccant and also its empty-

¹ Morley, E. W., *Am. J. Sci.*, **34**, 199 (1887); *J. Am. Chem. Soc.*, **26**, 1171 (1904); *J. chim. phys.*, **3**, 241 (1905).

² Willard and Smith, *J. Am. Chem. Soc.*, **44**, 2255 (1922).

³ Baxter and Starkweather, *J. Am. Chem. Soc.*, **38**, 2038 (1916).

⁴ Dover and Marden, *J. Am. Chem. Soc.*, **39**, 1609 (1917).

⁵ Baxter and Warren, *J. Am. Chem. Soc.*, **33**, 340 (1911).

⁶ McPherson, A. T., *J. Am. Chem. Soc.*, **39**, 1317 (1917).

⁷ Smith, G. F., *Ind. Eng. Chem.*, **19**, 411 (1927).

⁸ Walton and Rosenbaum, *J. Am. Chem. Soc.*, **50**, 1648 (1928).

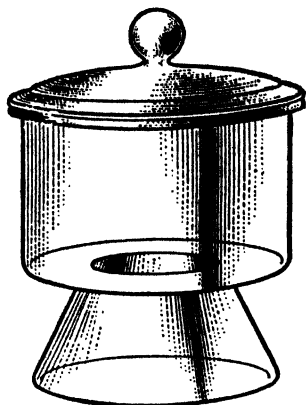


Fig. 1.—Scheibler Desiccator.

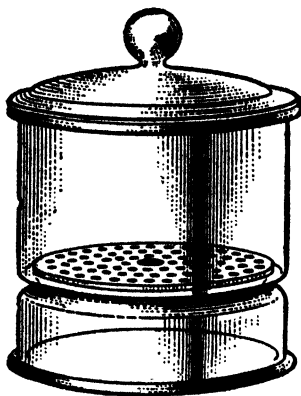


Fig. 2.—Frühling and Schultz Desiccator with Porcelain Desiccator Plate.

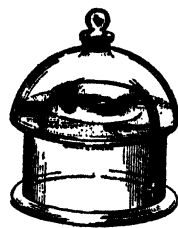


Fig. 3.—Hempel Desiccator, with Stoppered Tubulature.

ing. The Hempel desiccator,¹ in which the drying agent is placed in the upper part where the aqueous vapor tends to concentrate owing to the decrease in density of air with its degree of saturation, is shown in Fig. 3. The use of this type of desiccator facilitates the rate of drying.²

Drying at Low Temperatures in Vacuum.—The speed of drying in a desiccator may be greatly increased by exhausting the air contained therein. By this means the moisture diffuses more rapidly, and its rate of transfer from material to desiccant is hastened. The extent to which the material can be dried is not increased, however, since this is determined solely by the pressure of the water vapor in equilibrium with the desiccant. Vacuum desiccators are provided with tubulatures for connection with the vacuum pump. The Standardization Committee of the American Chemical Society recommends desiccators with the tubulature in the cover rather than the old-style vacuum desiccator with the tubulature in the side. In addition to vacuum desiccators of the three types described there has been recently introduced the Pyrex vacuum desiccator, which is made of extra heavy Pyrex glass with three glass lugs in the walls to support a desiccator plate; owing to its thermal resistance and mechanical strength it is the most satisfactory glass desiccator for vacuum. It is illustrated in Fig. 4 with a glass stopcock with a hook to hold a manometer as well as to direct the incoming air upward against the cover prior to opening,

¹ *Ber.*, **23**, 3566 (1890).

² Cooke and Richards, *Proc. Am. Acad. Arts Sci.*, **3**, 159 (1887).

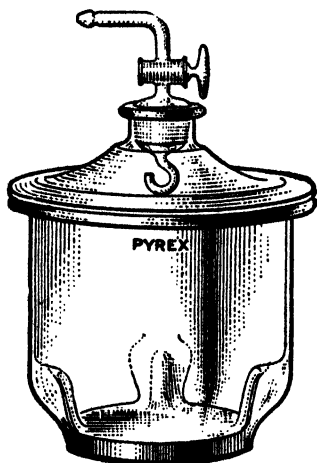


Fig. 4.—Pyrex Vacuum Desiccator with Stopcock Ground to Fit Tubulature.

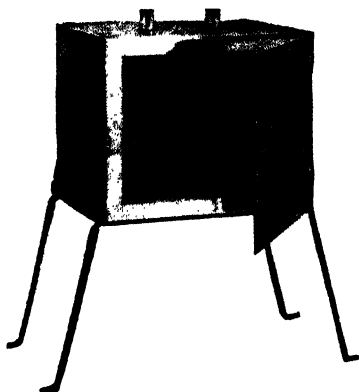


Fig. 5.—Single-Wall Drying Oven or Air Bath.

rather than upon the samples. In this way losses of material are prevented. The stopcock has been ground to fit the tubulature in the cover.

A means of securing a high vacuum in a desiccator when only a water pump is available has been published by Benedict and Manning.¹ This procedure may be briefly stated as follows:

Place fresh concentrated sulfuric acid (about 150 cc.) in the previously cleaned and dried upper compartment of a Hempel desiccator. After introducing the material to be dried (in appropriate containers), and just before the cover is put in place, deliver 10 cc. of pure anhydrous ether from a pipet upon the bottom of the desiccator, but do not allow it to come in contact with the material to be dried. Carefully adjust the cover, leaving the glass stopcock open. Connect the water pump immediately with the tube in the cover, and continue the exhaustion until the mercury manometer suspended from the hook in the desiccator shows from 40 to 60 mm. pressure. (A simple efficient manometer may be made from a 150 mm. length of small glass tubing sealed at one end and bent in a U-shape, and with the closed arm completely filled with clean mercury.) Close the stopcock, remove the tube connecting with the water pump and allow the desiccator to stand a few minutes, when a vacuum of from 4 to 1 mm. (or even less) is obtained.

If the stopcock and cover of the desiccator have been well fitted and well lubricated with a wax prepared by melting together 60-75 grams of beeswax, 15 grams of Venice turpentine and 15 grams of vaseline, the vacuum will hold indefinitely. The absorption of the ether vapor by the sulfuric acid may be considerably accelerated by so rotating the desiccator

¹ *Am. Chem. J.*, **27**, 340 (1902); *Am. J. Physiol.*, **13**, 309 (1905).

held in the hands as to agitate the acid and moisten a larger surface of glass in the top compartment. The advantages of this procedure are: (1) the apparatus required is that already in use in many laboratories, (2) the time required to secure a good vacuum is reduced to a minimum.

Drying at Higher Temperatures at Ordinary Pressures.—Drying of materials at higher temperatures is carried out in various types of ovens. The simplest of these, illustrated in Fig. 5, is the single-wall drying oven, or air-bath, usually constructed of copper. The plate of the wrought iron stand, on which the oven rests, protects the copper bottom from the flame of the gas burner. One of the two openings at the top is for the thermometer, while the other is for ventilation or a gas thermoregulator. The vessels containing the materials to be dried are placed on the perforated, removable shelves.

The double-wall drying oven is similar in general appearance to the single-wall, but it has a space between the outer and inner walls which can be used as an air jacket or be partially filled with water or other liquids. When the latter is done, the oven is called an oil, steam, glycerol, etc., bath, according to the liquid used. Constancy of temperature in the double-wall drying oven is maintained by means of a gas thermoregulator or by using liquids with constant boiling points. Thus a glycerine-water solution of specific gravity 1.19 at 15° C. will boil at 105° C. When the boiling point of a liquid serves to fix the temperature of the oven a condenser is frequently attached to the upper vent of the jacket to reflux the boiling liquid.

Within the last quarter century gas-heated ovens have been largely replaced in chemical laboratories by electrically heated ovens. They are usually equipped with electric thermoregulators in order to maintain any temperature within a rather wide temperature range automatically. One of the more commonly used types of electric ovens (Freas) is pictured in Fig. 6. It is constructed with a double wall of heavy asbestos transite, the space between the outer and inner walls being filled with air-cell asbestos. The frame, door and removable shelves are commonly made of cast aluminum. The heating element at the bottom of the oven, which consists of a wire-wound resistance plate, is easily removable. The openings in the side walls serve for ventilation and that in the top is for the insertion of a thermometer. The small electric lamp seen within the oven is used for illumination, and in conjunction with the small window in the door permits inspection of the interior without opening the door and resultant cooling of the chamber. The desired temperature is attained ap-

proximately by setting the pointer on the graduated temperature scale above the door, and final adjustment is made by comparison with the thermometer, which extends into the compartment.

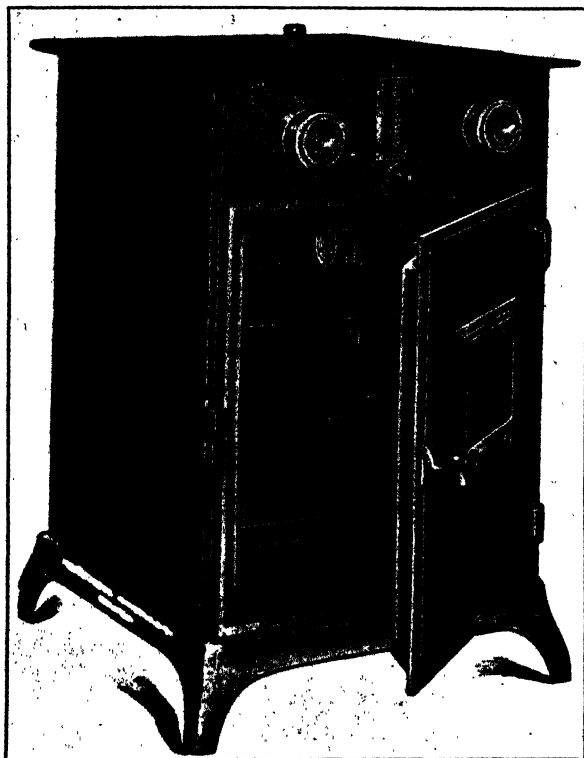


Fig. 6.—Freas Electric Oven.

Rapid drying may be accomplished by passing quickly through the material a relatively large volume of preheated air (or other gas). Fig. 7 shows an electric oven (Spencer) that has been devised for drying in this manner. The air is drawn through the lower end of the central brass cylinder, into which there is fitted a heating unit consisting of an alundum core wound with resistance wire, and is deflected by the top of the copper cover down through the four tared capsules that hold the material to be dried. These capsules are usually constructed of aluminum and are closed at the bottom with monel metal filtering cloth. The passage of the air

downward through the material prevents losses that might otherwise occur through mechanical suspension in the air current. The air and water vapor finally pass out through the channeled cast iron base plate into the tube shown at the side, which is connected with a water pump or other means for suction. One of the two openings in the top of the cover is

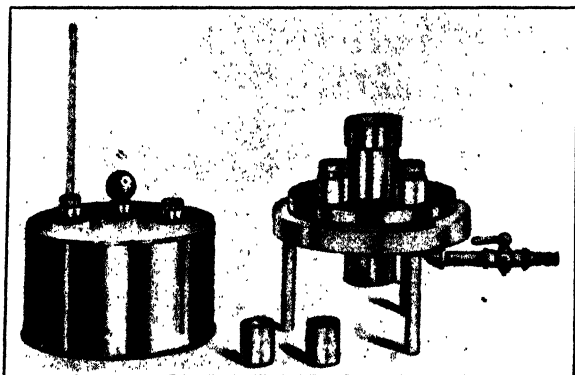


Fig. 7.—Spencer Electric Oven.

for a thermometer; the other is for a thermoregulator if the latter is desired. Liquids may be dried in this oven by first absorbing them in a carrier. This procedure may be combined with the vacuum in order to dry materials under reduced pressures in a current of heated gas. The passage of a current of dry air over samples being dried in any manner greatly facilitates the removal of moisture.

Extreme precaution should be taken in the use of electric ovens that are heated with the units within the drying chamber where known and constant temperatures for drying are required. When using an oven of the type shown in Fig. 6 Mitchell¹ found variations in temperature as high as 10°-15° C. in readings made every 5 minutes. Variations in temperature and differences in moisture results of samples placed in different parts of the oven indicated that no two places in the oven were heated alike and that the temperature was fluctuating continuously over a wide range. A similar condition showing the wide variation of temperature within an electric oven has been reported by the Bureau of Chemistry, U. S. Department of Agriculture, where it was observed that while a

¹ *J. Assoc. Official Agr. Chem.*, 5, 498 (1922).

thermometer in the center of the oven registered 100°C ., a thermometer lying on the porcelain plate at the bottom reached a temperature of 160°C . In a comparison of three electrically heated and controlled ovens, a gas-heated porcelain-lined oven, a gas-heated air-jacketed oven, a gas-heated constant-level water and steam jacketed oven, a steam-jacketed oven and a gas-heated constant-level water and steam-jacketed vacuum oven, Bailey¹ found that only those types surrounded by boiling water and steam were capable of maintaining even approximately uniform temperatures.

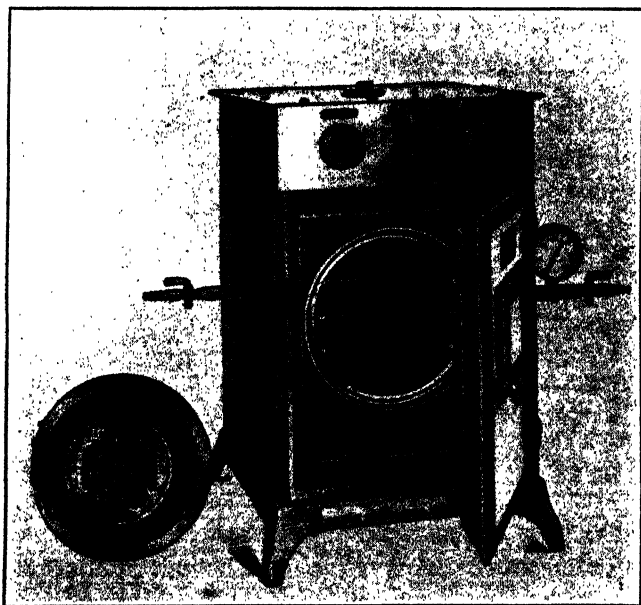


Fig. 8.—Vacuum Chamber Fitted into an Electric Drying Oven.

Drying at Higher Temperatures in Vacuum.—A vacuum is often used in drying materials at higher temperatures as well as at the lower temperatures. There are, however, additional advantages involved in the employment of a vacuum in connection with a drying oven, besides that of merely increasing the speed of drying as in a desiccator. The temperature at which the drying is conducted may be lowered considerably below 100°C . while still greatly reducing the time necessary for the moisture determination. The danger of charring is thus avoided and the pos-

¹ *J. Ind. Eng. Chem.*, **6**, 584 (1914).

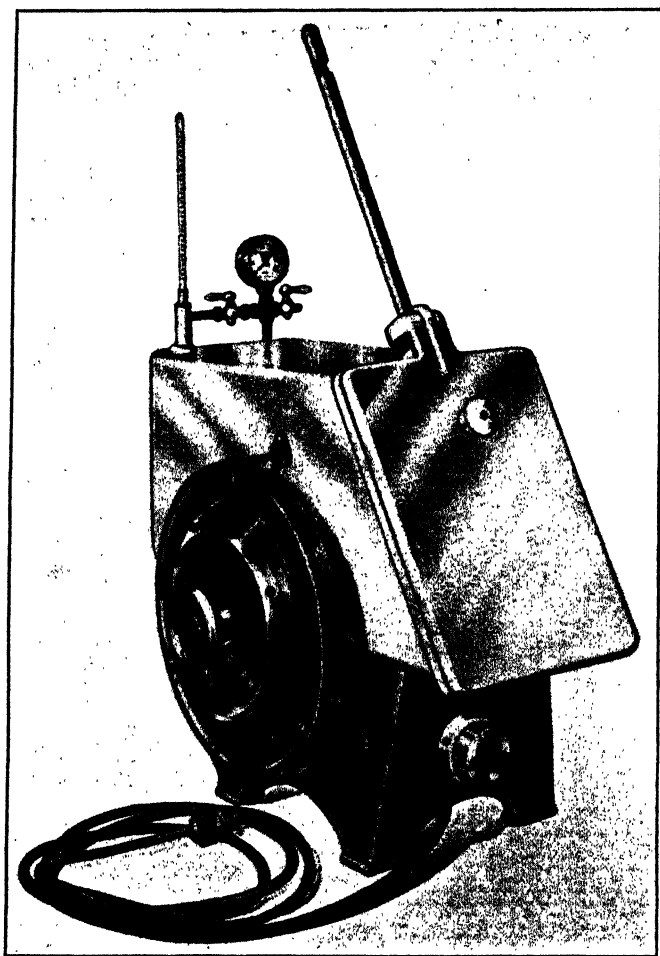


Fig. 9.—Mojonnier Electric Vacuum Oven.

sibility of the volatilization of other constituents lessened. Furthermore, the lower temperature and decreased oxygen pressure combine to limit oxidative effects. Fig. 8 shows a vacuum chamber fitted into an electric drying oven similar to that displayed in Fig. 6. The door of the chamber, which has been removed to disclose the interior with its shelves, has a central mica window that is reinforced by a heavy metal grid. This window permits observation of the chamber when the door has been

clamped into position since it is illuminated by means of an electric lamp situated behind a similar mica plate at the back of the chamber.

An electric vacuum oven (Mojonnier) of different type than that just described is shown in Fig. 9. The temperature within the oven is controlled by means of the rheostat attached to the side. This oven, which is essentially an electric hot plate enclosed in a vacuum chamber, can be used as an air-drying oven by opening the vent on the door or as a hot plate when the door is opened wide. The heating units are enclosed so that explosive or inflammable materials may be dried with greater safety. The inside compartment is 7 inches wide and 8 inches high.

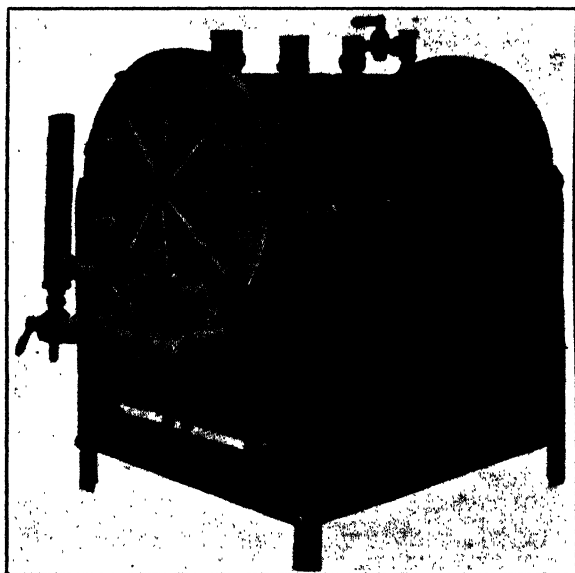


Fig. 10.—Double Wall Vacuum Oven.

A double wall vacuum oven for gas heating, as used by the Bureau of Chemistry and Soils, is shown in Fig. 10. The shell is made of heavy, seamless-drawn brass tubing jacketed with an inch space. The oven is provided with a constant water-level arrangement and with openings for exhaust from the chamber, a thermometer and a vacuum gage, and is supported by an iron frame incased in sheet iron. It contains two copper perforated trays or shelves. The two brass pipes (perforated) extending through the head may be used to moisten the material within the oven. There are also two burners for heating.

Drying at elevated temperatures is sometimes conducted in an atmosphere of a gas, such as hydrogen, nitrogen, carbon dioxide, or illuminating gas, in order to exclude the presence of oxygen. The vacuum ovens illustrated in Figs. 8 and 10 are well adapted to such tests as it is only necessary to pass a current of the gas through the vacuum chamber.

Miscellaneous Methods.—Many procedures for determining moisture depend upon other principles than the determination of the loss of weight upon drying. These methods, however, have not been applied generally in the estimation of the moisture in fertilizers, and mention only of them will be made here. They may be grouped in three classes: (1) densimetric and refractometric methods, (2) methods involving the direct measurement of the water collected after its distillation from the sample, and (3) methods in which the moisture is determined indirectly by the measurement of the quantity of gas formed by the reaction of the water with specific substances.

The densimetric and refractometric methods are commonly used in sugar work for the determination of total solids in sugar solutions. They are not applicable, however, to low-grade products such as molasses and other materials containing large quantities of non-sugar solids. The determination of total solids densimetrically may be made either by use of a spindle (hydrometer) or a pycnometer.

The determination of moisture by distillation and direct measurement of the collected water has found extensive application in the Duvel-Brown method for grain¹ and the Bidwell-Sterling method for various agricultural products.² In the Bidwell-Sterling method the sample is distilled with toluol, and the water is trapped in a calibrated tube.

A number of methods have been proposed involving the determination of the quantity of gas liberated by the reaction between certain added substances and the moisture in the material under examination. Thus Zerevitinoff³ advocated the treatment of the material with an alkyl magnesium haloid and measurement of the methane evolved, and Wilson⁴ used magnesium nitride, absorbed the ammonia in water and titrated with standard hydrochloric acid. The McNeil⁵ calcium carbide method in which the volume of the acetylene is measured directly was reported by Hilts⁶ to have too many sources of error to make it valuable as an absolute method.

¹ U. S. Patent 848,616. Brown and Duvel, March 26, 1907; Coleman and Boerner, U. S. Dept. Agr. Bull., **1375**, 1-44 (1927).

² *Ind. Eng. Chem.*, **17**, 147 (1925).

³ *Z. Anal. Chem.*, **50**, 680 (1911).

⁴ *J. Am. Chem. Soc.*, **43**, 704 (1921).

⁵ U. S. Dept. Agr. Bur. Chem. Cir., **97** (1912).

⁶ *J. Asso. Official Agr. Chem.*, **8**, 112 (1923).

OFFICIAL METHODS

The principles involved in the determination of moisture in different substances and the various general procedures followed in making such determinations having been discussed and outlined, a number of specific methods for the determination of moisture in fertilizers, most of which are considered official or have been legally prescribed as official methods in different countries, will now be given.

UNITED STATES

The original method of the Association of Official Agricultural Chemists for the determination of moisture in fertilizers was as follows:

(a) In potash salts, nitrate of soda, and sulfate of ammonia, heat 1-5 grams at 130° C. until the weight is constant, and reckon water from the loss.

(b) In all other fertilizers, heat 2 grams, or, if the sample is too coarse to secure uniform lots of 2 grams each, 5 grams for 5 hours at 100° in a steam bath.

This method, which was recommended for adoption in 1885,¹ has undergone practically no change since that time, as may be seen by comparison with the present official method.²

Heat 2 grams of the sample prepared under "Preparation of Sample—Official," for 5 hours in a water oven at the temperature of boiling water (98°-100° C.). In the case of potash salts, sodium nitrate, and ammonium sulfate, heat at about 130° C. to constant weight. Report the percentage loss in weight as moisture.

The limitation of the time of heating to 5 hours is obviously for the purpose of reducing the effects of the various disturbing factors already mentioned or to obtain a balance between them.

Owing to the varied nature of the materials used as fertilizers and in fertilizer mixtures, the analyst must exercise discrimination in his use of the official method and, in fact, of any other method for the determination of moisture in fertilizers. It would, for example, be folly to apply this method to diammonium phosphate, or mixtures containing it, and consider the loss in weight to represent water.

INTERNATIONAL METHODS

The following methods were proposed by the International Commission for the Analysis of Commercial Fertilizers and Feeds for the determina-

¹ U. S. Dept. Agr. Div. Chem. Bull., 7, 14 (1885).

² *Methods of Analysis*, A. O. A. C.

tion of moisture in commercial fertilizers and adopted by the Fifth International Congress of Applied Chemistry.¹

Ten grams of the material are taken and dried at 100° C. to constant weight; in cases where the fertilizer contains gypsum the sample is dried for 3 hours at that temperature. For potash salts the methods of the Kalisyndikat at Leopoldshall should be used.

The method of the Kalisyndikat² for the determination of water in potassium chloride and other concentrated potash salts referred to reads as follows:

Ten grams of the salt are heated for about 15 minutes at a low red heat in a covered platinum crucible over a small flame. In the case of salts containing magnesium chloride, loss of hydrochloric acid as a result of decomposition of the magnesium chloride according to the equation $\text{MgCl}_2 + \text{H}_2\text{O} = \text{Mg} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix} + \text{HCl}$ is avoided by mixing and covering the salt with freshly ignited lime or lead oxide. The loss of weight, determined after cooling in a desiccator, corresponds to the water content of the sample.

GERMANY

The following methods of the Union of Agricultural Experiment Stations in the German Empire are considered official in that country:³

The loss of weight at about 100° is considered ordinarily as water or moisture. For some substances special directions are given as follows:

Superphosphates and superphosphate mixtures.—For the moisture determination 10 grams of the sample are heated 3 hours at 100°. The loss of weight is considered as moisture.

Rock phosphates.—Drying at 100° should be used to determine the water content.

In addition to these official methods, those of the Union of German Fertilizer Manufacturers⁴ are also extensively used:

Conventional method.—For the determination of moisture about 10 g. are weighed out and dried in weighing glasses at 100° to constant weight. In the case of materials containing gypsum these are dried 3 hours at this temperature. The temperature must be kept closely. In the case of materials that contain other volatile substances, these are determined separately and their weight subtracted from the total loss of weight. In this procedure the chemically combined water of gypsum and of the calcium monophosphate is always partially included in the result.

¹ Proc. 5th Internat. Cong. App. Chem., Vol. 1, p. 228.

² Laboratoriumsbuch für die Kaliindustrie, 2nd edit. L. Tietjens. Halle (Saale), 1924.

³ Landw. Vers. Sta., 39, 337 (1917).

⁴ Methoden zur Untersuchung der Kunstdüngemittel. Braunschweig. 1925.

The determination of moisture in the superphosphates should be carried out with these spread out in a thin layer in wide weighing glasses.

For the determination of water in Chile saltpeter 10 grams of the sample that has been ground and sieved as quickly as possible are dried for 2 hours at 130° to 140°.

For the determination of water in crude potash salts 10 g. are covered in a platinum crucible with a weighed layer of ignited lead oxide and heated at a dull red heat for 10 minutes over a small flame, the cover of the crucible being on. The loss of weight as a result of the ignition gives the water content; or 10 g. are ignited and the loss of weight is determined, the ignited mass is dissolved in water and the chlorine content ascertained by titration in order to determine how much magnesium chloride was decomposed by the ignition. The difference between the chlorine contents of the ignited and non-ignited sample is deducted from the loss in weight on ignition, consideration being taken of the amount of oxygen taken up. The difference is the water.

To determine the moisture in lime fertilizers, 10 g. are dried 3 hours at 100°. For the determination of the water of hydration 1 to 2 g. of material are ignited in a combustion tube through which a current of dry air is passed and the water is caught in a weighed calcium chloride tube, or 1 g. of the material is ignited in a tared platinum crucible (with cover) for 5 minutes in a blast. The loss of weight is due to water, organic matter and carbon dioxide. The difference, after subtraction of the amount of carbon dioxide as found by analysis, is considered as water.

A method that is claimed to determine hygroscopic moisture only in superphosphates is that of L. Schucht.¹

To 2 grams of the superphosphate sample in a 6 cm. glass dish with a pourout are added 20 cm. of absolute alcohol. The mixture is frequently stirred with a small glass or agate pestle and permitted to stand for an hour. It is then decanted upon a filter paper which has been previously dehydrated with absolute alcohol and ether, dried at 40° C. and weighed. Suction is applied, and the contents of the dish are transferred to the filter paper, washed with alcohol and then with ether until the alcohol has been removed.

The filtrate is evaporated on a water bath and dried in a drying oven at 120° C. until constant weight (a) has been reached, which requires about 3 hours. In order to get a constant weight it is necessary to place the container with its contents as quickly as possible in a desiccator after its removal from the drying oven, letting it cool there, and obtain a first approximate weight, then to repeat the drying and weighing.

The filter paper, with its contents, is placed on a tared watch glass, freed from ether in a drying oven at 40° C., and weighed (b).

The percentage of moisture in the superphosphate is given by the equation:

$$\text{Percentage of H}_2\text{O} = \frac{2 - (a + b)}{2} \times 100.$$

¹ Die Fabrikation des Superphosphates. Verein Deutscher Dünger-Fabrikanten. Braunschweig. 1926; Laboratoriumsbuch für Agrikulturchemiker. Gustav Metzger. Halle (Saale), 1926.

This method avoids heating the monocalcium phosphate and gypsum in the superphosphate above 40° C. and thus driving off water of crystallization from these salts.

An approximate determination of the dry matter in urine or liquid manure may be obtained by evaporating about 10 grams of the material upon the water bath and then drying the residue for 3 hours in a drying oven at 105° C. In this procedure, however, some urea is decomposed, and in the case of not entirely fresh urine the ammonium carbonate, which it contains as a result of the fermentation of urea, volatilizes. The escape of the ammonia can be prevented by the addition of a weighed quantity of tartaric acid¹ (at most 5 times the weight of the total nitrogen contained in the sample taken for the determination)² before the evaporation. When the weight of the added tartaric acid is subtracted after the heating the result is more accurate, because it is increased by the weight of the ammonia, which would have been volatilized without the addition of the tartaric acid.

The addition to stable manure of a solution of tartaric acid of known content so as to give it a slightly acid reaction likewise prevents the loss of ammonia in the drying of this material. The use of oxalic acid instead of tartaric acid has also been recommended to prevent the volatilization of ammonia in making moisture determinations. The employment of sulfuric acid, which is sometimes advocated, is not advisable because it may attack organic matter and any excess causes trouble in drying. Also, if the manure contains any nitrates or nitrites, loss of nitrogen results. This has not been found to occur when tartaric acid is used.

Another method that is used when ammonia may be liberated from the material during drying is as follows:³

Five grams of the material are weighed into a tared porcelain boat, which is then introduced into a glass tube passing through an oven. One end of the tube is connected with a tube containing calcium chloride or a flask containing concentrated sulfuric acid, which dries the air drawn through the train; the other end is connected with a bulb-apparatus which contains a known volume of a standard solution of sulfuric acid (preferably one-tenth normal). Drying is brought about by drawing by suction a slow current of air through the tube, heated to 100° C., for 1 to 2 hours, or until the porcelain boat and its contents reach a constant weight. The quantity of ammonia that has been driven off is determined by titration and subtracted from the loss in weight to obtain the actual moisture content. If am-

¹ Stohmann, F., *Z. anal. Chem.*, **3**, 197 (1864); Pfeiffer and Thurmann, *Landw. Vers. Sta.*, **40**, 18 (1896).

² Hugo Neubauer, *Analyse der Düngemittel*. Berlin, 1925.

³ Stohmann, F., *Anleitung zur quantitativen Analyse*, 1857, p. 719.

monium carbonate is lost the ammonia absorbed in the standard acid is calculated to ammonium carbonate before the subtraction.

A German procedure for the determination of moisture in Chile saltpeter or potassium nitrate is to heat the sample carefully in a covered platinum crucible to incipient fusion, after which it is allowed to cool in a desiccator and weighed.¹ Drying 3 hours at 130° C., and drying to constant weight in a vacuum desiccator over phosphorus pentoxide² are also methods recommended as giving accurate results with these salts. Although the odor of iodine is sometimes detectable when Chile saltpeter is thus heated, due to the reduction of potassium iodate, the iodine content of this salt is said to be of no practical significance and not to influence the result. E. Dinslage³ claims that heating calcium nitrate in a platinum crucible for a short time over the low flame of a Meker or similar burner gives reliable results for the determination of water in this fertilizer salt.

ENGLAND, SCOTLAND AND IRELAND

The following method is prescribed by statutory order:⁴

A weighed quantity of the sample shall be dried at 100° C.

AUSTRIA

The Union of Agricultural Experiment Stations in Austria adopted the following as official methods on December 6, 1926:

In superphosphates.—Dry 10 g. 3 hours in a water-filled drying oven. State the loss of weight.

In other fertilizers.—Dry 10 g. of the material in an air bath 3 hours at 120° C. The determination of water in phosphorites should be made according to established custom (dry 10 g. 3 hours in a water-filled drying oven). Potash salts must be heated 10 minutes at a low red heat. Salts containing MgCl₂ require a layer of lead oxide spread over them.

NORWAY

The State Chemical Agricultural Stations use the method proposed in 1924 by a committee appointed for the purpose of formulating uniform methods of analysis for fertilizers and feeds:

5 g. of the substance are dried 4 hours at 103°–105° C.

¹ Metge, G. *Laboratoriumsbuch für Agrikulturchemiker*, Halle, 1926.

² Koenig, J. *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*, Berlin, 1923.

³ *Chem. Ztg.*, **35**, 1045 (1911).

⁴ Statutory Rules and Orders, No. 421, 1928. London.

SWEDEN

These instructions for determining water in fertilizers are included in the Royal Agricultural Board's regulations relating to work at the state-subsidized chemical stations:

In general the determination of water in fertilizer materials or the like is made so that after 3-5 g. of the sample have been weighed into a drying dish (of at least 5 cm. diameter and at most 2 cm. height) this is heated in an oven at 98°-103° to constant weight or till the loss of weight after a two hour drying amounts to not more than 2-3 mg. The drying oven should be provided with an arrangement for sufficient ventilation.

In potash salts the water content can be determined by ignition to about 500° (scarcely visible, initial red heat). But since hydrochloric acid can escape when hydrous magnesium chloride is ignited, a correction must be made, in the case of salts containing magnesium chloride, for the loss of the hydrogen chloride in order to secure an accurate determination, for example by determining the chlorine in the sample before and after the ignition.

DENMARK

The methods laid down for the examination of fertilizers in conformity with the State law include the following for the determination of water:

In superphosphates.—5 g. are dried 3 hours at about 100°. The loss of weight is given as water content.

In Thomas Phosphate meal, bone meal, mineral phosphate (apatite, phosphorite or the like) and lime fertilizers.—5 g. are dried at about 100° to constant weight.

In potash fertilizers.—10 g. are ignited in a covered platinum crucible at a dull red heat for 10 minutes. The loss of weight is given as water. In the case of salts that contain magnesium chloride determine the loss of chlorine caused by the ignition by a titration with 0.1 normal silver nitrate solution before and after the ignition. The loss minus the weight of the equivalent quantity of oxygen is subtracted from the loss on ignition before calculating the percentage water content.

In Chile saltpeter, ammonium nitrate and ammonium sulfate.—2-5 g. are dried at about 100° to constant weight. The loss of weight is given as water.

In organic nitrogenous fertilizers.—5 g. are dried 3 hours at about 100°. With such fertilizers as may contain ammonium carbonate (*e. g.*, guano, blood meal) carry out the water determination in the following manner:

1-2 g. substances are placed in a small porcelain or platinum boat and dried to constant weight, the boat being inserted in a cylindrical glass tube which passes through the water bath with boiling water. A stream of air which has passed through concentrated sulfuric acid and dehydrated calcium chloride in order to free it from ammonia and moisture is drawn, during the entire drying process, over the material and then through 0.1 normal acid. The loss of weight of the substance weighed out is determined and from it is subtracted the weight of the ammonia taken up by the acid, the ammonia being calculated as ammonium carbonate.

ITALY

The Laboratories of the Italian Customs Department determine moisture in fertilizers in accordance with the following directions given in a Manual of Technological Analytical Chemistry:¹

General Methods.—From 5 to 10 grams are heated at 100° to constant weight. Superphosphates and other products rich in gypsum are dried in a boiling water oven for 4 hours.

If the fertilizer has an alkaline reaction or it is feared that ammonia may be lost during the drying, as, for instance, with stable manure, the fertilizer (5 grams) is placed in a tared porcelain boat and this is introduced into a glass tube arranged in a suitable oven. One end of the tube is connected with a wash-bottle containing concentrated sulfuric acid and the other with a bulb-tube charged with 20 or 25 cc. 0.1 *N* sulfuric acid. The oven is heated to 100° and during the drying a slow current of air is passed through the glass tube. The boat is finally reweighed and the loss of weight diminished by the weight of ammonium carbonate corresponding with the ammonia absorbed by 0.1 *N* sulfuric acid.

If the fertilizer has an acid reaction and it is feared that loss of volatile acid or changes rendering the estimation inaccurate will occur in drying, the fertilizer is first neutralized. To this end 5 grams are weighed in a weighing bottle, tared together with a thin glass rod. The mass is then moistened and neutralized with normal caustic soda solution. That neutralization is approaching is indicated by the ready clarification of the supernatant liquid and the exact point determined by touching litmus paper with the rod. The liquid is then evaporated to dryness and the crust broken with the rod, drying being then continued for a further period of 4 hours. Each cc. of normal caustic soda added increases the weight of the dry matter by 0.022 gram.

Special Methods.—*Ammonium Sulfate.*—5 grams are heated at 110–120° to constant weight.

Sodium Nitrate.—As for ammonium sulfate. The nitrate may also be weighed in a crucible, heated carefully to incipient fusion, allowed to cool in a desiccator and reweighed.

Potash Salts.—10 grams are heated at a dull red heat in an open platinum crucible for 10 minutes. If the salt contains magnesium chloride, it is covered with a layer of ignited quicklime.

Water in Stable Manure.—250–500 grams are dried at 70–80° for some hours and then left to cool in the air and weighed. The dried mass is then cut into small portions, chopped and reduced to a fine powder, which is thoroughly mixed again. 10 grams of this are then heated at 105° until of constant weight, the total moisture being calculated.

In order to avoid any loss of ammonia, the total water may be determined as indicated under "General Methods."

¹ See Villavecchia, V. *Treatise on Applied Analytical Chemistry*. Philadelphia, 1918.

CANADA AND INDIA

The methods of the Association of Official Agricultural Chemists for moisture determinations are used in these countries.

NEW ZEALAND

The regulations under the Fertilizers Act, 1927,¹ require that—

A weighed quantity of the sample shall be dried at 100° C. to constant weight.

¹ *New Zealand Gazette*, No. **72**, 1928.

CHAPTER IV

PHOSPHORIC ACID

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SOURCES AND PREPARATION

The principal sources of the phosphatic materials that are used in fertilizers are bones, iron ores, guanos and mineral phosphates.

The use of bones as a fertilizer is a practice of long standing, and their value in increasing crop yields was early appreciated in many climes by many races of people. Although certain mineral phosphates are similar to bones in that they contain a high percentage of calcium phosphate, their value for fertilizer purposes was not recognized until about 1842. The utilization of basic slag recovered in the manufacture of steel from phosphorus-rich ores was a development of a still later date. Guano was extensively used in the early development of the fertilizer industry, but the supply is now relatively small.

Since bones and basic slag are recovered as by-products in industrial operations, their production can not be increased independently of the principal product. The continuous increase in the demand for phosphatic fertilizers is therefore being largely supplied by the mineral phosphates, and the consumption of these materials is greatly in excess of the output from all other sources.

BONES

Fresh raw bones are composed mainly of moisture, alkaline earth phosphates, fats and cartilaginous matter with small proportions of calcium carbonate and alkali salts. The bones of young animals contain more cartilage than those of old animals, but the reverse is true of their phosphate content. The percentage of fat in the different bones of the body varies considerably, and the bones of mature animals contain more than those of partially grown animals.

The fatty matter of bones decreases their value for fertilizer use because it retards their decomposition in the soil and interferes with the absorption of water by plants. It is therefore usually extracted and used

for other purposes. The cartilaginous matter is also frequently removed in the treatment of bones for fertilizer manufacture because it increases the difficulty of grinding the bones and is more valuable for the preparation of glue than as a source of plant food.

The most efficient process for removing the fat from bones consists in extracting with a solvent, such as benzine, having a boiling point between 100° and 133° C. The fat may also be removed by digesting the crushed bones with steam in a closed vessel at a pressure of 15-20 pounds, or by subjecting them to successive digestions with steam and extractions with hot water. This treatment removes not only the fat which separates out in a molten condition, but also the cartilage which passes into solution as gelatin. The two products may be separated by centrifuging or other means. Degreased and degelatinized bones may thus be prepared in one operation or in two separate steps.

Bone products appearing in the fertilizer trade are conveniently classed as follows:

1. Ground raw bone.—This product is prepared by drying and grinding animal bones not previously steamed under pressure, and contains the whole of the material including fat and gelatin.

2. Bone meal.—Bone meal differs from ground raw bone in that it has been treated with a fat solvent such as benzine. The fat content of the original bone has therefore been removed but the cartilage remains.

3. Ground steamed bone.—This product is prepared by grinding bones that have been previously steamed under pressure for the purpose of removing the greater part of the fat and gelatin. It is usually ground to pass a 50-mesh screen. Its phosphoric acid content is more readily soluble than that of bone meal.

4. Dissolved bone.—Dissolved bone is ground raw bone, or meal, that has been treated with sulfuric acid. This manner of treatment, which is much the same as in the manufacture of superphosphate from phosphate rock, was first tested out in Germany in 1841, at the suggestion of Liebig, and the following year it was applied independently by Lawes in England on a commercial scale. The use of sulfuric acid in the treatment of bone represents the first step in the development of a commercial fertilizer industry. Dissolved bone has not been regularly produced in the United States for a number of years.

5. Bone charcoal.—Bone charcoal, or bone black, is the name given to the residue that remains after bones have been submitted to destructive distillation in an air-tight retort. In common with other charcoals it has a marked absorptive capacity and is used in the purification and clarification of sugar juices and other liquids. After long use as a clarifying agent it loses its effectiveness and is then said to be "spent." The spent charcoal contains a higher percentage of carbon than the freshly prepared bone charcoal. It makes an excellent raw material for the manufacture of phosphoric acid or high-grade superphosphate.

6. Bone ash.—Bone ash is the mineral matter that remains after bones have been burned. Large quantities were at one time imported from Argentina and other South American countries where the practice formerly prevailed of burning bones for fuel. The supply at present has been largely exhausted. Bone ash makes an excellent superphosphate. It also finds a ready market in the manufacture of high-grade phosphoric acid and other phosphatic products.

7. Precipitated bone phosphate.—Precipitated calcium phosphate is a by-product obtained in one of the processes now in use for the preparation of glue from bone. The bones are first degreased and then immersed for several days in a dilute acid solution such as 8 per cent hydrochloric acid. The mineral matter is dissolved by this treatment, but the cartilaginous matter is left undissolved. The solution obtained is transferred to a precipitating tank, and sufficient milk of lime is added to precipitate the phosphate in the solution as dicalcium phosphate. The precipitate is filtered off, washed to remove the calcium chloride and dried in a current of warm air. The dried product is in the form of a friable powder containing 30-40 per cent phosphoric acid (P_2O_5).

Typical analyses of different bone products are given in Table I.

TABLE I.—COMPOSITION OF TYPICAL SAMPLES OF BONE PRODUCTS.

Constituent	Raw bone	Bone meal	Steamed bone	Bone charcoal	Bone ash
	Per cent	Per cent	Per cent	Per cent	Per cent
Moisture	8.0	7.0	13.5	20.6	17.4
Organic matter	36.1	32.6	9.9		
Lime, CaO	28.0	29.9	40.0	41.3	39.7
Magnesia, MgO	0.6	1.0	1.0		
Phosphoric acid, P_2O_5	21.0	21.5	30.1	32.3	32.6
Carbonic acid, CO_2	1.2	3.2	0.5	2.3	0.8
Alkali salts	0.2	0.2	0.2		0.8
Silicious matter	1.7	1.4	1.0	2.6	6.5

IRON ORES

Iron ores are divided into two classes, Bessemer and non-Bessemer, according to their phosphorus content. This classification was adopted at a time when steel was made by the acid Bessemer process, and no method was known for the removal of phosphorus. A phosphorus content in excess of 0.1 per cent renders a steel brittle and undesirable for many industrial purposes, and no ores that gave a pig iron containing more than 0.1 per cent of phosphorus could therefore be used. Practically all the phosphorus in the ore passes into the pig iron. A Bessemer ore is therefore one which does not contain over 0.001 per cent of phosphorus for each per cent of iron in the ore.

Basic Slag.—Attempts to utilize non-Bessemer ores by bringing about a removal of the phosphorus in the process of smelting proved unsuccessful

owing to the high reducing conditions necessary in the blast furnace for the recovery of the iron from the ore. A new process for converting the pig iron into steel and simultaneously removing the phosphorus was finally developed in 1878 by two English chemists named Thomas and Gilchrist. This process, known as the basic Bessemer process, consists in lining the Bessemer converter with a basic lining composed of lime and magnesia, adding lime to the charge, and blowing a blast of air through the molten metal. The phosphorus in the metal is oxidized to phosphoric acid (P_2O_5), which in turn combines with the added lime to form a slag. This product, known as basic slag, proved to be an excellent fertilizer.

In the basic Bessemer process, the air that is blown through the molten charge supplies the oxygen necessary for the purification of the metal while the high temperature required is obtained from the combustion of the phosphorus, carbon and other impurities present. A relatively high proportion of phosphorus may, therefore, be desirable because it reacts with oxygen and serves to maintain the necessary temperature.

The situation is somewhat different in the basic open-hearth furnace which is largely replacing the Bessemer converter. Here the heat is largely supplied from an outside source, and upwards of two-thirds of the oxygen required for the oxidation of the impurities is derived from the iron ore that is charged with lime into the heated furnace before the addition of the pig iron. The presence of phosphorus in the iron offers no advantage in this process and low-phosphorus ores are preferably used. This fact, coupled with the greater quantity of slag produced, makes the open-hearth slag as a rule inferior and more variable in composition than that produced by the basic Bessemer process.

Basic open-hearth and basic Bessemer slags may also differ greatly in the availability of the phosphorus as measured by the citric acid test (p. 114). This difference is due to the practice that has been adopted in many open-hearth plants of adding fluorspar to the charge for the purpose of increasing the fluidity of the slag and aiding in the process of desulfurizing. The reduced solubility of the phosphoric acid in the slag is due to a combination of the fluorspar with the calcium phosphate to form artificial apatite.¹

Basic slags, as produced and marketed for fertilizer purposes, are classified by Russell² into three groups: (1) High-grade basic Bessemer slags containing about 20 per cent P_2O_5 (85 per cent or more citric acid-

¹ Bainbridge, *Trans. Faraday Soc.*, **16**, 302 (1921).

² *Ibid.*, **16**, 263 (1921).

soluble); (2) open-hearth basic slags containing from 7 to 14 per cent P_2O_5 (85 per cent or more citric acid-soluble); and (3) open-hearth basic slags containing from 7 to 10 per cent P_2O_5 (20 per cent or less citric acid-soluble).

A number of well-defined phosphate minerals have been found in basic slag, but the effective fertilizer component of this product is considered to be a complex compound of tetracalcium phosphate and monosilicates, of the general formula $(CaO)_4P_2O_5 \cdot (RO)_2SiO_2$, RO being either CaO, MgO, MnO, or FeO.¹

Table II gives the composition of some typical basic slags.

TABLE II.—COMPOSITION OF BASIC SLAGS FROM DIFFERENT SOURCES.

	Basic Bessemer			Basic Open Hearth Fluorspar Slag		Non-fluorspar Slag	
	England ¹	Germany ¹	Canada ²	United States ³	Canada ²	United States ³	Canada ²
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Lime, CaO	49.40	45.64	42.57	46.00	55.50	47.76	47.25
Magnesia, MgO	3.97	2.19		7.43		5.90	
Ferrous oxide, FeO	7.89	1.13	22.60				
Ferric oxide, Fe_2O_3	7.44	15.63		10.72	10.98	17.31	14.24
Alumina, Al_2O_3	1.06	1.17					
Manganous oxide, MnO	4.61	6.61		2.27		2.27	5.67
Sulfur, S.	0.44	0.13					
Sulfuric acid, SO_3	0.21	0.31		0.35		0.40	
Phosphoric acid, P_2O_5	18.38	18.32	16.85	9.62	13.00	16.60	13.95
Silicic acid, SiO_2	6.77	7.61	10.75	22.96	10.83	8.96	11.28

¹ Feilitzen and Lugner, *Chem. Ztg.*, **37**, 689 (1913).

² Private communication, Dominion Iron and Steel Co., Sydney, N. S.

³ Private communication, Tennessee Coal, Iron and Railroad Co., Birmingham, Ala.

The availability of the phosphorus in basic slag increases with the fineness of grinding and with the silica content and decreases as the fluorine content increases. According to Kaysser,² the availability is also materially affected by the rate at which the material is cooled after being tapped from the furnace. Slags that are rapidly cooled are hard, but they show higher availability than those that are allowed to cool slowly in block.

Considerable attention has been given to the problem of increasing the availability of phosphatic slags to which fluorspar has been added, but all attempts in this direction have so far been unsuccessful. Basic slag produced by the basic Bessemer process may be enriched by adding phosphate

¹ Cf. Colclough, *J. Iron Steel Inst.*, **107**, Part 1, 267 (1923).

² *Chem. Ztg.*, **44**, 826 (1920).

rock to the charge in the blast furnace or in the converter, but this is not practicable in the open-hearth process. Adding finely ground phosphate rock to the slag as it is tapped from the furnace for the purpose of bringing about a reaction between the rock and molten slag does not increase the availability of the phosphorus in the mixture sufficiently to make the process an economic one.

The most effective method for enriching open-hearth slag involves a duplex treatment in the production of the slag. This process, which is applicable in the manufacture of low carbon, high phosphorus steels, was developed by the only concern¹ in this country producing high-grade slag. In the first step of the process, the minimum quantity of lime required to give a high phosphorus content in the final slag is charged into the furnace along with scrap and ore. When this charge is brought to the proper temperature, blown metal from an acid converter is added to complete the charge and the molten metal is worked down to a suitable carbon and phosphorus content. On tapping, a considerable portion of the metal and most of the slag is left in the furnace. In the second step a large addition of blown metal is made to the furnace, causing a reaction and the transfer of a greater portion of the phosphorus from the metal to the slag. The furnace is then tilted, and as much slag as possible is taken from the fore-plate in front of the furnace. This slag is high in phosphorus and is handled separately from other slags. Lime and ore additions are then made to the furnace to form a new slag, and blown metal is added to complete the change. The metal is worked down to the specifications, tapped as in the first step, and the process is repeated. The production of slag by this process is limited by the demand for high-phosphorus steel.

Table III shows variations in the availability of basic slag prepared by different methods. Availability tests on phosphate rock are also included for comparison.

Wheeler² states that basic slag made without fluorspar is an effective source of phosphoric acid for use upon all kinds of soil and that owing to its free lime and carbonate content it is of special promise for the reclamation of acid soils, particularly such as are rich in organic matter, like many marsh or muck soils. It has also proved very beneficial to clover, alfalfa and the grasses. Fluorspar slags give somewhat increased yields, but they are less effective than the more soluble slags.³

¹ Tennessee Coal, Iron and Railroad Co., Birmingham, Ala.

² U. S. Dept. Agr. Farmers Bull., **77** (1905).

³ Bainbridge, *Carnegie Fellowship Memoirs*, 1919, 1-8; 1920, 1-40; Russell, *Trans. Faraday Soc.*, **16**, 263 (1921).

TABLE III.—TOTAL AND CITRIC ACID-SOLUBLE P_2O_5 IN BASIC SLAGS AND ROCK PHOSPHATE.

Material	Place of manufacture	Total P_2O_5	Available P_2O_5 as determined —by Wagner method using—			
			5 gram sample	1 gram sample	5 gram sample	1 gram sample
		Per cent	Per cent	Per cent	Per cent	Per cent
Basic Bessemer Slag ¹	England	17.19	14.64	85.2	16.35	95.2
Basic Bessemer Slag ¹	Belgium	14.24	13.49	94.7	13.68	96.1
Basic Bessemer Slag ²	Canada	16.85	16.65	98.8		
Basic Open Hearth Slag ³	Canada	12.96	10.22	78.8		
Basic Open Hearth Slag ⁴	United States	16.60	13.37	80.5		
Basic Open Hearth Fluorspar Slag ²	England	9.20	1.61	17.5	1.68	18.3
Basic Open Hearth Fluorspar Slag ³	Canada	11.30	1.80	15.9		
Basic Open Hearth Fluorspar Slag ⁴	United States	9.62	6.60	68.6		
Florida Rock Phosphate ²		33.19	6.06	18.2	20.88	62.6
Tunisian Rock Phosphate ²		26.21	10.05	38.3	23.36	89.1
Algerian Rock Phosphate ²		29.32	9.79	33.4	24.22	82.6

¹ Shutt, Report of the Dominion Chemist, 1925, p. 21.² Robertson, *Trans. Faraday Soc.*, **16**, 291 (1921).³ Private communication, Dominion Iron and Steel Co., Sydney, N. S.⁴ Private communication, Tennessee Coal, Iron and Railroad Co., Birmingham, Ala.

Table IV gives the production of basic slag in the different slag-producing countries throughout the world.

TABLE IV.—WORLD PRODUCTION OF BASIC SLAG IN METRIC TONS.¹

Country	1913	1916	1919	1922	1925	1926	1928
Germany	2,702,000 ²	1,800,000	700,000	1,178,925	1,315,000	1,397,000	1,639,000
Belgium	655,000		380,000	475,000	545,788	722,704	955,625
France	730,000		202,508	611,820	1,136,200	1,224,412	1,475,000
Great Britain	404,000 ³	508,000 ³	519,135 ³	305,830	269,252	187,969	221,498
Luxembourg	250,000	232,338	75,842	375,900	462,695	528,386	632,775
Poland	164,267			40,009	20,725	71,568	3,312
Saar	393,000			206,081	250,000	282,507	329,983
Sweden	18,354	13,258	11,725	7,527	6,784	12,430	9,496
Czechoslovakia					138,241	126,132	154,932
Canada				8,330	2,024	4,393	
United States ⁴				14,744	10,582	19,438	18,144

¹ Intern. Yearbook, Agr. Statistics, 1909-1921, p. 457; 1925-1926, p. 491; 1929-1930, p. 569.² Including Saar.³ Including Ireland.⁴ Private communication, Tennessee Coal, Iron and Railroad Co.

GUANOS

The word guano is derived from the Peruvian word "huanu," meaning excrement. The guanoses of commerce may be conveniently divided into (1) bird guano or guano proper, (2) phospho-guano, and (3) bat guano.

Bird guano.—Bird guano is composed chiefly of the excrement and remains of fish-eating birds and was formerly found in great abundance in numerous arid islands off the Peruvian coast and in other maritime localities. As now marketed it contains an average of about 12.5 per cent of nitrogen and about 10 per cent of phosphoric acid (P_2O_5). It is, therefore, of more value as a source of nitrogen than of phosphoric acid, and is properly classed as a nitrogenous fertilizer.

Phospho-guano.—The phospho-guanos, on the other hand, contain only 1 to 2 per cent of nitrogen, while their P_2O_5 content may reach a maximum of 40 per cent or more. The phospho-guanos were formed by weathering of the nitrogen-rich guanos and are found in localities where the rainfall is sufficient to bring about decomposition of the organic constituents of the guano and the loss of nitrogen as ammonium salts. Guanos high in phosphorus are found on islands off the west coast of South America and Africa, in some of the West Indian Islands and in the Gulf of California.

Bat guano.—Bat guano is formed from the droppings and remains of bats. The largest deposits of this material are found in limestone caves in arid or semi-tropical countries, such as Mexico and Southwestern United States. Analyses of a large number of samples collected in Porto Rico showed a nitrogen content varying from practically 0 to 13.0 per cent and a P_2O_5 content ranging from less than 1 per cent to 41.58 per cent.¹

TABLE V.—COMPOSITION OF GUANO.

Constituents	Peruvian guano ¹	Phospho-guano ¹ — Gulf of California		Fresh bat guano, on dry basis ²
	Per cent	Per cent	Per cent	Per cent
Moisture	2.35	4.83	9.33	
Organic volatile matter	63.75	12.72	4.28	83.65
Nitrogen, N	17.03	1.04		10.25
Phosphoric acid, P_2O_5	9.09	34.33	34.83	6.95
Lime, CaO	10.14	37.36	42.21	2.36
Magnesia, MgO	2.65	1.76	0.59	1.40
Ferric oxide, Fe_2O_3	trace	0.50		0.38
Potash, K_2O				3.85
Alkali salts	7.38	5.54	4.82	
Carbonic acid, CO_2		0.46	3.05	
Sulfuric acid, SO_3				3.00
Silica, SiO_2	4.64	1.69	0.89	0.16

¹ Lambert, Bone Products and Manures, 3rd Ed., pp. 151, 154.² Gile and Carrero, *loc. cit.*

The average annual production of Peruvian guano during the past five years is in the neighborhood of 100,000 tons, of which about 20,000 tons were exported. The annual importations of Peruvian guano into the United States varied from a maximum of 163,662 tons in 1854 to about 8,000 tons at the present time.

The composition of a number of typical guanos is given in Table V.

MINERAL PHOSPHATES

CLASSIFICATION

Phosphorus is found in nearly all igneous rocks and ranks twelfth in abundance among the elements of the earth's crust. With one or two exceptions of minor importance it exists in the mineral kingdom only in the form of phosphates, of which a large number are known. These phosphates may be conveniently divided into two classes, crystalline and non-crystalline.

The *crystalline phosphates* are limited in extent, and apatite alone of the minerals of this class has been used as a source of phosphoric acid. Apatite is a phosphate of calcium of somewhat variable composition, containing chlorine or fluorine, or both. Two varieties of the mineral, known as chlorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{Cl}]$ and fluorapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$, are recognized.

Apatite is found in all classes of rocks, but it occurs principally as veins or intrusions in igneous rocks. The largest deposits are found in Canada, Spain and Norway. Some of these deposits were formerly worked on a fairly large scale, but the cost of mining due to the irregularity and uncertainty of the deposits and to the hardness of the country rock has greatly decreased the production.

Although apatite is of little application at present in the manufacture of phosphatic fertilizer, it is widely distributed in soils derived from igneous rocks, and being somewhat soluble in the percolating soil water it serves as an important source of phosphorus for growing crops.

The *amorphous or non-crystalline phosphates* belong to a class of rock-forming minerals known as phosphorite or phosphate rock. They resemble apatite in that they are phosphates of calcium and so far as known all contain fluorine. The phosphorites are by far the most important of the mineral phosphates, and the present production of phosphatic fertilizers from this source greatly exceeds that from all other sources combined.

The origin of these deposits has been a matter of considerable speculation, and numerous theories have been advanced to explain their sources

and mode of formation. It is now generally agreed that the coprolites of England are fossilized excrements of prehistoric animals and that the deposits found on numerous tropical islands throughout the world are derived from the guano and remains of birds which fed on marine life. Opinions respecting the origin of the large deposits of the United States and Northern Africa are much more divergent. According to Clark¹ they have their origin in the phosphates dissolved in sea water. These phosphates are deposited in the calcareous shells, bones and tissues of marine animals, and after the death of these animals become concentrated in the sediment at the bottom of the sea. The carbon dioxide formed by the decomposition of the animal matter assists in further concentrating the phosphates by increasing the solubility of the calcium carbonate with which the phosphate is associated. When any portions of the sea bottom in which these sediments have accumulated are elevated into land surfaces further concentration of the phosphate occurs through the relatively greater solubility of the associated calcium carbonate in the ground water. Leaching of the phosphates by percolating water also occurs with formation of secondary deposits as a result of the redeposition of the dissolved phosphates in the underlying limestones or in limestone caverns.

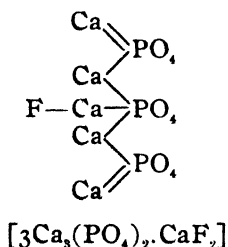
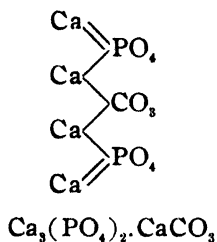
Phosphate deposits may thus be formed by the direct accumulation of the bones, shells and excrements of animals, by secondary replacements, or by deposition from solution; and may undergo concentration by mechanical washing and by removal of the accompanying limestone by leaching.

The presence of fluorine in all phosphate deposits is thought to be due to the agency of percolating water carrying small quantities of fluorides. It occurs principally as a constituent part of the phosphate molecule, but it may be present as calcium fluoride. Analyses by Reynolds, Jacob and Hill² of 56 samples of commercial rock from Florida, Tennessee, Idaho, Wyoming and Northern Africa showed a fluorine content varying from 3.22 to 4.28 per cent. The results indicate that the ratio of F to P_2O_5 in Florida pebble rock decreases with the increase in the P_2O_5 content of the rock, but that the ratio is approximately constant in different grades of Florida hard-rock, Tennessee brown and blue rock and Western phosphate. The Ocean Island phosphates as a rule contain a lower proportion of fluorine than the commercial grades from other sources.

¹ U. S. Geol. Survey Bull., **491**, 500 (1911).

² J. Assoc. Official Agr. Chem., **11**, 237 (1928); Ind. Eng. Chem., **21**, 1253 (1929).

Phosphate rock frequently occurs in association with calcium carbonate deposits, and the ratio of CO_2 to P_2O_5 in rock samples may therefore vary in all proportions. Calcium carbonate may also occur in phosphate rock as a constituent part of the molecule. The composition of this compound and of the corresponding fluorine compound may be represented graphically as follows:



Natural calcium phosphates also contain other complex compounds in which a part of the fluorine may be replaced by chlorine or the hydroxyl group.

The ratio of calcium to phosphoric anhydride in all these compounds is greater than that corresponding to the normal tricalcium phosphate and so far as known no deposits of the tri-phosphate occur in nature. It is customary however in the phosphate rock industry to consider the calcium phosphate as tricalcium phosphate and to so represent it in the equations of chemical reactions involved in the manufacture of available phosphates.

Magnesium is found in phosphate rock both as the carbonate and phosphate, while sulfur is present as pyrite and calcium sulfate.

Iron occurs in phosphates mainly as the phosphate. It may also be present as pyrite or in the form of oxides and silicates. Aluminum is also present as silicate but chiefly as phosphate. The presence of more than 2 per cent of combined iron and aluminum, expressed as the oxides, is considered objectionable in a phosphate intended for use in the manufacture of superphosphate, although rock phosphates containing as much as 4-6 per cent of these oxides are actually being used for this purpose. Many phosphate deposits are known, however, which carry a combined iron and aluminum content greatly in excess of the maximum limit allowable for superphosphate manufacture. This is particularly true of the phosphates occurring in the islands of Redonda and Alta Vela of the Lesser Antilles group. These deposits consist largely of the hydrated phosphates of iron and aluminum, particularly the latter. As the lime in

these phosphates is small, amounting to 1 per cent or less, they are not usually considered as belonging to the phosphorite, or calcium phosphate, class of rock-forming minerals.

Redonda phosphate contains on an average about 38 per cent phosphoric acid (P_2O_6), 22 per cent alumina, 10 per cent iron oxide and 22 per cent free and combined water.¹ Attention has been given to the possible utilization of this material by igniting it with alkali salts and other reagents for the production of alkali phosphates and aluminum compounds, but none of the methods so far proposed is sufficiently economical to compete with phosphate production from other sources.

The principal phosphate deposits of the world, in decreasing order of importance, are found in the United States, Northern Africa, a number of tropical islands, and Europe.

PHOSPHATES OF THE UNITED STATES

The principal phosphate rock deposits of the United States are found in Florida, Tennessee and the western states of Utah, Idaho, Wyoming and Montana. Deposits of less importance also occur in South Carolina, Kentucky and Arkansas.

Florida.—The deposits of Florida have been exploited since 1888, and the output since that time has exceeded that of any other phosphate field. The phosphate rock mined in Florida is of three types, known as hard rock, land pebble and soft phosphate.

The hard rock region lies towards the west side of the peninsula and extends in a north and south direction from Suwannee and Columbia Counties, to Citrus and Hernando Counties, a distance of over 100 miles. The rock occurs as nodules or boulders in irregular pockets which vary in size from a few square yards to several acres in extent; it is hard and compact with a fine homogeneous grain and white or pale yellow in color. The beds vary greatly in thickness, ranging from five feet or less to upwards of 50 feet. The percentage of P_2O_5 in run-of-mine rock ranges from less than 10 per cent to more than 30 per cent. The deposits are covered with an overburden of sand and clay varying from a few inches to 30 feet or more in thickness, and rest on a light-colored limestone of lower Oligocene age.²

The rock is mined by first removing the overburden with steam shovels and then digging out or dredging the phosphate thus exposed according

¹ Tate, *J. Soc. Chem. Ind.*, 5, 570 (1886).

² Waggaman, U. S. Dept. Agr. Bur. Soils Bull., 76, 1-23 (1911).

to whether the deposit is above or below the normal water table. Dry mining is performed by hand labor or with steam shovels and blasting is often resorted to. Dredge mining is more expensive because selective mining is then not possible and the cost of equipment is somewhat greater.

The mined material is shipped in tram cars to the washing plant, where it is passed through a grating and subjected to such a rubbing, washing, and screening operation that adhering sand, clay and soft phosphates are separated from the rock and carried in suspension in the washing water to waste ponds at some distance from the plant. The washed material is passed in turn to picking tables where lumps of non-phosphatic materials are removed by hand and to rotary kilns where it is finally dried. The dried product is sold on a guarantee of 77 per cent of tricalcium phosphate with a maximum of not more than 3 per cent of combined iron and aluminum oxides and 4 per cent of moisture.

The marketable materials recovered in the washing process seldom exceed 15 per cent of the total material mined. The remaining 85 per cent, consisting of sand, clay and fine particles of relatively high-grade rock, is discharged into the waste pond. This discarded material contains on an average about 10 per cent of P_2O_5 . It follows, therefore, that the quantity of phosphoric acid lost in the refining of the phosphates must be about 50 per cent greater than the quantity actually saved.

The production of hard rock has decreased during the past two years, owing to the relatively high cost of producing a marketable product and to the competition of the North African fields.

The pebble phosphates of Florida have been more extensively mined than any other source. Those that occur on river bottoms are known as river pebbles, while those that have not been exposed to the action of any water are called land pebbles. The principal pebble phosphate mines are in Polk and Hillsboro Counties, about 20-40 miles east of Tampa.

The pebble phosphates are imbedded in a matrix of sand and clay somewhat similar to that in which the hard rock is found, but the yield of product per ton of material mined is considerably greater than in the case of the hard rock phosphate. The workable deposits range in thickness from a few feet to upwards of 20 feet, with an average of 12 feet. These deposits are therefore more regular in their occurrence than those in the hard rock region. The overburden ranges from a few feet to 40 feet, with an average thickness of about 15 feet. The pebbles have rounded outlines produced by mechanical erosion, and range from small granules to pebbles about two inches in diameter with an average diameter of less

than 1 inch. They vary in color from light gray to black.

The system of mining pebble phosphates differs from that employed in the hard rock fields in that the cheap hydraulic method is almost universally employed. After the removal of the overburden, heavy streams of water are made to play upon the phosphate material, which is washed into a sump and sucked through pipes to the washing plant by means of centrifugal pumps.



Fig. 1.—Hydraulic Mining of Florida Pebble Phosphate.

Courtesy of the Coronet Phosphate Company.

The washing and the screening treatment, to which the pebble phosphate is subjected in the refining process, is similar to that employed in the hard rock district but the nature of the material is such that the loss of phosphate is much less. Several grades are marketed. The grade containing 66-68 per cent tricalcium phosphate is used in the domestic trade, while the higher grades containing 75-77 per cent are shipped abroad.

The Florida soft phosphates occur principally in association with the hard rock from which it may be recovered as a by-product in the washing process. This type of phosphate is a clay-like material which is plastic when wet but can be readily crushed to fine powder when dry. Lumps of the dried material readily disintegrate in contact with water, and as much as 65 per cent may be of a colloidal nature.¹ Its alumina content is

¹ Jacob, Hill and Holmes, *Colloid Symposium Annual*, 7, 195-204 (1929).

too high to make it of practical application at present in the manufacture of superphosphate, but it has been used to some extent for direct application to the soil. There is still considerable difference of opinion, however, as to its economic value when used for this purpose, owing to the low availability of its phosphoric acid and its relatively high cost to the consumer. As placed on the market at present it contains about 20-25 per cent of phosphoric acid (P_2O_5).

Tennessee.—The Tennessee deposits rank second in importance among the phosphate fields of this country. They occur in what is known as the Central Basin of Tennessee. The mines that are being worked at present occur in Lewis, Maury, Hickman, Davison and Giles Counties, but deposits have also been mined in Williamson, Perry and Decatur Counties. These deposits are of three different types, known as the brown, blue and white phosphates.

The brown rock occurs in rocks of Ordovician age. It is generally conceded that it is formed from phosphatic limestone by the leaching out of the more soluble calcium carbonate. The highest grade deposits are therefore found in localities such as the northwest region in Maury County where conditions are favorable to the leaching action of percolating water. The rock consists of brown or gray plates which form beds ranging in thickness from a few inches to upwards of 25 feet, with an average of 6-8 feet. The thickness of the overburden varies greatly and may exceed that found in the Florida fields.

The methods of mining and washing the Tennessee brown rock are similar to those employed in the Florida hard rock fields but the nature of the product is such that the loss of phosphatic material is much less.

The brown rock of Tennessee is characterized by a higher iron content than the Florida rock. The better grades will analyze as high as 78 per cent tricalcium phosphate, but the average grade is about 72 per cent and contains approximately 5 per cent of the combined oxides of iron and aluminum. Some of the higher grade rock as well as lower grades containing a relatively high percentage of iron and aluminum are marketed for direct application to the soil. When used for this purpose the material is dried and ground to such a degree of fineness that a considerable proportion will pass a 300-mesh screen. Many experiments have been made on the agricultural value of the finely ground raw rock phosphate, and the work is still in progress. It has been found that best results are obtained when the rock is mixed in with the soil rather than simply broadcasted on the surface. The fineness of grinding and the presence in the

soil of fairly large quantities of organic matter are also important factors in determining the effectiveness of raw phosphate fertilization. It is generally recognized, however, that ground phosphate, irrespective of the degree of fineness, is not so quickly available as the more soluble phosphates.

The most important blue rock mines are found in Hickman and Lewis Counties; other deposits occur in the western part of Maury County.

The blue rock is tough and granular and resembles limestone. It belongs to the Devonian period and occurs in distinct strata which are blue, black or gray in color. The workable beds vary from $1\frac{1}{2}$ to 4 feet in thickness. According to Hayes and Ulrich,¹ these deposits were derived from the underlying Ordovician limestone and from the remains of marine life, which were considered to be more highly phosphatic, and they were subjected to less leaching action than were the brown rock deposits.

The blue rock deposits are overlain by massive blue-black shale or slate, 3 feet or more in thickness, which necessitates the adoption of underground methods of mining. The rock is mined by blasting and stripping around the face of the hill and by subsequently adopting the same operations that are generally employed in mining any flat lying deposits that are covered with an overburden too thick to be economically removed.

The texture of the blue rock prevents the removal of impurities by washing. The operations employed in the preparation of the material for market—mining, crushing and screening—are therefore different for the most part from those practiced in the Florida fields. Although some specimens of blue phosphate run as high as 80 per cent tricalcium phosphate, the average grade of rock is not usually more than 68 per cent. The combined iron and aluminum present is usually less than that in the brown rock. The iron is generally present in the form of pyrite.

The white phosphates, like the hard rock deposits of Florida, occur in irregular pockets along with clay and other materials. They are therefore not being mined at present. The deposits that were formerly exploited occur in Perry and Decatur Counties; they are all of a secondary nature and are supposed to be of comparatively recent origin. The three classes recognized are known as the stony, breccia and lamellar varieties. The last-mentioned is the richest of the three varieties and is the only one that has been mined commercially. It is considered to be somewhat higher grade than the Tennessee blue rock, but mining operations were discontinued in 1908 owing to the high cost resulting from the loose character

¹ U. S. Geol. Survey, Columbia Folio 95 (1903).

of the overlying clay, the hardness of the rock, and the uncertain character of the deposits.

Utah, Idaho, Wyoming and Montana.—The phosphate deposits in the western part of the United States underlie immense areas in the section comprising southeast Idaho, western Wyoming, northern Utah and western Montana. The western phosphates are of the Carboniferous age and occur in both Mississippian and Permian rocks. They differ materially in their physical properties and mode of occurrence from the other deposits of the United States, and most resemble the blue rock of Tennessee. The color of the rock is generally gray, brown or black. Its characteristic oolitic texture may be lacking when the grain of the rock has been destroyed by pressure. When struck, the rock yields a penetrating fetid odor like that of crude petroleum. There is no correlation, however, between the odor of the rock and its phosphoric acid content. The richer beds range from 2 to 9 feet in thickness and contain from 65 to 75 per cent of tricalcium phosphate with less than 3 per cent of the combined oxides of iron and aluminum. The fluorine content of western rocks is much the same as that of the phosphate deposits in other parts of the country, amounting to approximately 3.5 per cent in marketable grades of rock. They differ from other commercial rock in that they contain from 0.1 to 0.2 per cent chromic oxide (Cr_2O_3) and from 0.1 to 0.5 per cent vanadium pentoxide (V_2O_5). These constituents give a green color to solutions of the rock in sulfuric acid. Western rock is also characterized by a relatively high content of organic matter, as indicated by the analysis given in Table VII, which shows an ignition loss of 7.2 per cent. The moisture in the rock, as it comes from the mine, varies from 4 to 6 per cent.

The western phosphate deposits are the most extensive yet discovered, but development has been limited owing to their great distance from the fertilizer market. The deposits so far developed are mined by underground methods. A considerable proportion of the rock contains such a high percentage of iron, aluminum and calcium carbonate as to make its use impracticable in the manufacture of superphosphate.

South Carolina, Kentucky and Arkansas.—The phosphate deposits of South Carolina were first worked in 1868 and are thus the oldest phosphate rock mines in this country. For many years they furnished the bulk of the supply of phosphate rock used in the United States and in many countries of Europe. The production decreased from a peak in 1893 until 1922, when mining operations ceased altogether owing to the

exhaustion of the more readily available rock and to the marketing of higher grade rock from other sources.

The South Carolina phosphate beds belong to the Tertiary Period, and according to Waggaman¹ have an average thickness of only about one foot. The rock occurs as boulders or nodules embedded in a matrix of sand or clay similar to the Florida hard rock, and a similar washing process is therefore required to prepare the rock for market. The color of the rock varies from gray to black.

The phosphate deposits of Kentucky and Arkansas are not generally regarded as of much economic importance, and no commercial production from these states has been reported since 1926.

PHOSPHATES OF NORTHERN AFRICA

The principal phosphate-producing countries of Northern Africa are Tunis, Morocco, Algeria and Egypt. In 1927 these countries produced approximately 53 per cent of the world's phosphate, and the United States produced about 32 per cent; the remaining 15 per cent was divided among 22 countries.

Tunis.—The development of the Tunisian phosphate deposits began about 1899. Production increased from 70,000 metric tons the same year to 3,074,950 tons in 1927. Tunis thus ranks next to the United States among the phosphate-producing countries of the world.

The deposits of Tunis are of Eocene origin and occur in strata from 15 to 115 feet in thickness. The most important commercial deposits are in the vicinity of Gafsa, near the Algerian border. The Société de Phosphate de Gafsa is the largest single producer of phosphate rock in the world. The rock averages 58-68 per cent of tricalcium phosphate with 2 per cent of the combined oxides of iron and aluminium. The workable layers are 5 to 8 feet thick, and lie nearly horizontal under the hills on a level with the valleys at the sides. The rock is mined underground by the same methods that are used in French coal mines and requires no washing. As it comes from the mines it is slightly damp and is either dried in the sun or passed through rotary kilns. When the rock is shipped approximately 50 per cent will pass a 60-mesh screen; it is very soft, and the color varies from a light gray to brown. Efforts are being made to increase the quality of the rock by air concentration.

Morocco.—The occurrence of phosphate rock in Morocco was not discovered until 1912, and development work did not begin until about 5

¹ U. S. Dept. Agr. Bull. 18, 1-12 (1913).

years later. The growth of the industry since that time has set a record that may not be surpassed, having increased from an output of 33,000 tons in 1921 to 1,400,000 tons in 1927.

The principal deposits are located in the central part of the northwest coast region about 60 miles from Casa Blanca, a seaport on the Atlantic coast. The rock is gray, fragile and easy to grind; much of it is in powdered form and requires little or no treatment to prepare it for market. The beds lie near the surface and are said to total from 24 to 300 feet in thickness. The thickness of individual beds may exceed 8 feet. Large tonnages which contain 70 per cent or more of tricalcium phosphate are available. The high quality of the run-of-mine rock and the low cost of mining and preparing the material for market account for the rapid development of the industry in this field.

Algeria.—The Algerian deposits were discovered in 1873 and were the first to be developed in Northern Africa. They are a continuation of the Tunisian deposits and are therefore of the same general character and age. The most important mines are located near the town of Tebessa in Northeastern Algeria, about 100 miles from the Mediterranean Sea, but other important deposits at present unexplored are known to exist further inland. The phosphates in the Northeastern field occur in a basin-shaped deposit composed of five separate beds. The workable beds vary from about 2 feet to 9 feet in thickness and are chiefly mined by open cuts, although underground mining is also practiced. No washing of the rock is required as in the case of the Florida deposits, and preparation for the market consists merely in the simple operation of drying and crushing. The Algerian rock averages approximately 65 per cent of tricalcium phosphate.

Egypt.—Phosphate rock was first discovered in Egypt on the east branch of the Nile in 1897. Other deposits yielding a higher grade product have also been located near the coast of the Red Sea. The Egyptian deposits are considered to belong to the Cretaceous age, and are therefore geologically older than the deposits of Tunis and Algeria. They are similar in character to the other deposits of Northern Africa but vary more in thickness and general appearance. The Egyptian phosphates are light in color and sufficiently friable to be readily crushed. Deposits have been worked which contain as high as 75 per cent of tricalcium phosphate, but the marketable grades usually range from 58 to 68 per cent tricalcium phosphate with a combined iron and aluminum oxide content of 1-3 per cent. The

phosphorite obtained from the Kosseir deposits¹ contains up to 72 per cent of tricalcium phosphate and 13-15 per cent of calcium carbonate. It is applied directly to acid soils in Italy as a source of both lime and phosphoric acid.

PHOSPHATES OF THE TROPICAL ISLANDS

The principal phosphate-bearing islands are Nauru, Ocean, Makatea, Angaur, Gilbert and Ellice Islands in the Pacific Ocean, Christmas Island in the Indian Ocean, and Aruba and Curaçao Islands in the Caribbean Sea. The phosphate deposits on these islands are the richest in the world, having a content of 80-88 per cent of tricalcium phosphate. It is generally conceded that these deposits, like the phospho-guano beds of Peru, had their origin in guano that was deposited by birds which fed on marine life and lived, bred and died on the islands. There is evidence that the islands have been submerged on several occasions, with the result that all soluble constituents in the guano were washed away, while the phosphates were fixed by the underlying coral formation in the form of high-grade calcium phosphate. The birds responsible for these deposits are now extinct, and the islands today are rarely visited by birds.

Nauru is a small isolated island in the Southern Pacific, about 26 miles south of the equator. The phosphate deposit on this island has little or no overburden, and is almost pure white; it is mined by pick and shovel and frequently has to be dug from around coral pinnacles. A deposit is usually abandoned after a depth of 20-30 feet between the pinnacles has been reached and before the phosphate has been exhausted, owing to the cost of mining to a greater depth.

Ocean Island is about 200 miles southeast of Nauru Island and is about one-third its size. The phosphate beds extend to a depth of 50 feet and are usually covered with a light overburden. They are similar in grade and occurrence to those found on Nauru Island.

The phosphates of Christmas, Makatea, Angaur and Curaçao Islands are also similar to those of Nauru Island, but they are slightly lower grade, averaging about 80 per cent of tricalcium phosphate. The first of the islands mentioned is in the Indian Ocean, about 190 miles southwest of Java; the second is a small island of the Society group, about 120 miles north of Tahiti; the third is one of the Pellew Group, about 800 miles east

¹ Chiappelli, *Girn. risicoltura*, **10**, 156 (1928); **19**, 171 (1929).

of the southern end of the Philippine Islands; and the fourth is an island of the Dutch West Indies.

PHOSPHATES OF EUROPE

The principal phosphate-producing countries of Europe are France, Belgium, Russia and Spain. All the European deposits are too low grade to compete successfully in international commerce with the higher grade phosphates found in other parts of the world. At one time during the early history of the fertilizer industry, Belgium, England and France produced a considerable tonnage of low-grade rock for use in the manufacture of superphosphate, but the industry in these countries has since greatly declined or ceased altogether.

The Belgian deposits occur either as nodules embedded in a matrix of clay or as beds of phosphatic chalk in Tertiary and Cretaceous strata. The grade of rock now available averages only 40-45 per cent tricalcium phosphate and is therefore not suitable for direct use in the manufacture of superphosphate. A small tonnage, however, is used for this purpose after mixture with the proper proportion of high-grade rock from other sources. The phosphates of France are similar in grade and occurrence to those of Belgium and are used in a similar way.

The phosphates of England are of interest in that they owe their origin to the excreta of prehistoric animals. The most productive beds are from 8 to 12 inches thick and consist of dark brown or black nodules. The average grade of this phosphatic material, known as coprolite, is below 50 per cent and it contains too high a percentage of iron to be used in superphosphate manufacture unless it is mixed with higher grade material.

The deposits of Spain, and particularly of Russia, are more extensive than those of the other European countries, but all are classed as low grade, and the production is relatively small.

WORLD PRODUCTION OF PHOSPHATE ROCK

The production of phosphate rock in the United States exceeded that from any other source from 1888, when the Florida fields were developed, until 1922, when North Africa took the lead. Table VI shows that the output at present from the North African fields exceeds that from all other sources combined.

TABLE VI.—WORLD'S PRODUCTION OF PHOSPHATE ROCK.¹

(In metric tons)						
Country	1900	1910	1915	1920	1925	1928
Florida	652,635	2,062,375	1,433,895	3,423,463	2,976,990	2,929,746
Tennessee	458,095	447,722	389,994	645,037	484,734	586,362
South Carolina	420,682	204,580	79,804	44,849	2,181	
Western States					73,797	41,521
Other States	20 830	10 258		56,502		
United States	1,552,242	2,724,985	1,903,692	4,169,851	3,537,702	3,557,629
Tunis	171,288	1,286,262	1,389,074	1,075,180	2,691,000	2,789,000
Morocco					692,181	1,337,100
Algeria	270,920	319,069	225,891 ⁴	502,931	815,116	875,947
Egypt		2,397	82,998	114,813	106,808	200,563
Africa	442,208	1,607,728	1,697,963	1,692,924	4,305,105	5,202,610
Nauru and Ocean Islands		310,625	92,000	300,000	478,278 ²	509,971 ⁴
Gilbert and Ellice Islands					213,405 ²	
Christmas Island	(2)	310,625	24,118	70,690	111,829 ⁴	113,687 ⁴
Makatea Island			71,724	30,000 ⁴	81,061 ⁴	136,606 ⁴
Aruba and Curaçao Island (2)		31,408	83,915 ⁴	61,486	81,771 ⁴	104,194 ⁴
Angaur Island		45,000	30,000	30,000	60,963	65,000
Other Islands	2,230	6,816	15,714	30,187	24,193	32,597
Ocean Islands					1,051,500	
Belgium	215,670 ³	202,880	16,350	133,040	15,125	15,510
France	587,919	333,506	145,000	124,930	225,565	
Russia	25,663	15,293		375	36,067	75,000
Spain	4,170	2,840	9,080	42,896	5,315	7,897
Other Countries	930	993	1,901	6,861	2,834	22,859
Europe	834,352	555,422	172,331	308,102	284,906	
Asia		1,042	57,723	110,540	119,115	79,223

¹ *Mineral Ind.*, 1902, p. 516; 1906, p. 638; 1913, p. 575; 1917, p. 517; 1918, p. 553; 1922, p. 553; 1923, p. 527; 1926, p. 512; 1928, p. 474; 1929, p. 483.

² Statistics not available.

³ Cubic meters.

⁴ Exports.

⁵ Exports during fiscal year ending June 30 of year named.

COMPOSITION OF ROCK PHOSPHATE

In Table VII analyses are given of representative samples of phosphate rock from different sources. Many of the results given for fluorine are open to question, because it is now known that the methods in use at the time the analyses were made gave low results.

TABLE VII.—COMPOSITION OF MINERAL PHOSPHATES.

Constituent	A	B	C	D	E	F	G	H
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Moisture	1.46	0.72		none	1.90	1.10	1.25	0.28
Combined water and organic matter								
Phosphoric acid, P_2O_5	3.39	3.28	4.90	2.78	1.83		7.20	
Lime, CaO	38.24	27.27	30.01	35.11	31.09	35.51	32.00	39.24
Magnesia, MgO	52.38	46.13	48.55	52.60	44.77	42.80	44.20	55.70
Ferric oxide, Fe_2O_3	1.35	2.02	1.02	0.40	1.00	0.30	0.47	0.20
Alumina, Al_2O_3	1.01	2.59	0.60	0.30	1.42	2.75	0.53	0.72
Potash, K_2O			0.85	0.50	2.13	1.70	1.20	
Soda, Na_2O			0.14	0.14	0.28		0.14	0.80
Chromic oxide, Cr_2O_3			1.48	0.62	0.60		0.42	
Vanadium pentoxide, V_2O_5							0.07	
Carbonic acid, CO_2	1.69	6.70	4.31	2.50	3.32	1.65	0.16	
Sulfuric acid, SO_3			3.25	1.21	1.36	1.89	1.78	
Chlorine, Cl			0.16	0.01				0.65
Fluorine, F			0.98	2.43	3.53	1.49	1.10	3.10
Silica, etc.	0.28	8.12	4.20	2.32	7.85	4.70	5.60	0.06

A. Makatea Island Phosphate—Robertson, *J. Agr. Sci.*, **8**, 16 (1916).

B. Algerian Phosphate, *ibid.*

C. Tunisian Phosphate—Berthon, *Les Réserves Mondiales en Phosphates*, p. 630. Grafías Reunidas, S. A., Madrid. 1928.

D. Morocco Phosphate, private communication.

E. Florida Pebble Phosphate, analysis by authors.

F. Tennessee Brown Rock, private communication.

G. Western Rock Phosphate, *ibid.*

H. Canadian Apatite—Spence, *Les Réserves Mondiales en Phosphates*, p. 684. Grafías Reunidas, S. A., Madrid. 1928.

WORLD RESERVES OF PHOSPHATE ROCK

An estimate of the reserves in the principal phosphate deposits of the world is given in Table VIII. The figures indicate that the United States has about 38 per cent of the total world reserves and about 60 per cent of the world's reserve of phosphates containing more than 60 per cent of tricalcium phosphate.

At the Fourteenth International Geological Congress at Madrid in 1926, estimates were submitted for the phosphate rock reserves of various countries in Europe, Africa and Asia. These estimates differ greatly from those given in Table VIII. Thus the phosphate rock reserves for Spain and Russia in Europe are reported to be respectively, 263,000,000 and 15,839,000,000 metric tons; for Japan, 25,078,000 metric tons and for Morocco and Tunis in Northern Africa, 300,000,000 and 451,000,000,000 metric tons.¹

¹ *Les Réserves Mondiales en Phosphates*, pp. 35, 43, 57. Grafías Reunidas, S. A. Madrid, 1928.

TABLE VIII.—WORLD RESERVES OF PHOSPHATE ROCK.¹

(In metric tons)

Country	Reserves	Estimated tricalcium phosphate content	
		Per cent	
Idaho	5,169,257,000		
Montana	397,584,000		
Utah	331,973,000		
Florida	298,704,000		
Wyoming	117,594,000		
Tennessee	85,300,000		
Arkansas	20,320,000		
South Carolina	8,941,000		
Kentucky	892,000		
United States		6,431,000,000	60-70+
Algeria	1,452,000,000		58-68
Morocco	1,400,000,000		70-78
Tunis	1,000,000,000		58-68
Egypt	179,000,000		60+
Northern Africa		4,000,000,000	60-78
Nauru Island	100,000,000		80-88
Ocean Island	50,000,000		80-88
Makatea Island	10,000,000		80+
Angaur Island	3,000,000		80+
Rasa Island	3,000,000		75
Pacific and Ocean Islands		166,000,000	75-88
Palestine	4,000,000		47-80
<i>Total High-Grade Rock</i>		10,622,000,000	
Russia	5,568,000,000		Less than 50
Spain	10,000,000		Less than 50
Europe		5,578,000,000	
Siberia	667,000,000		Less than 50
Japan	3,000,000		Less than 50
Asia		670,000,000	
<i>Total Low-Grade Rock</i>		6,248,000,000	

¹ Mansfield, World Conditions as to Mineral Raw Materials for the Fertilizer Industry, pp. 94-6. National Fertilizer Association, Washington, 1926; Waggaman and Easterwood, Phosphoric Acid, Phosphates and Phosphatic Fertilizers, pp. 87-9. The Chemical Catalog Co., New York, 1927.

PROCESSED ROCK PHOSPHATES

The different processes that are used or have been proposed for increasing the availability of phosphate rock as a fertilizer may be conveniently divided into two classes, (1) those in which the rock is treated with an acid, and (2) those in which the rock is calcined with an alkali or alkaline earth

salt. The principal products formed by treatment with acid are superphosphate, double superphosphate and precipitated or dicalcium phosphate. The products formed by calcination are sold under trade names such as "Tetraphosphate," "Rhenania Phosphate" and "Calcined Phosphate."

SUPERPHOSPHATE

The preparation of superphosphate by treating bones with sulfuric acid was first proposed by Liebig in 1840. The process was later extended to include the mineral phosphates in a British patent [Brit. Pat. 9353 (1842)] granted to Lawes in 1842. The commercial development of the process was immediately undertaken by Lawes, and the following year production of superphosphate began at Deptford, England. The most available phosphorite deposits known at that time, the coprolites of Suffolk and Cambridge, were the first to be used in the manufacture of superphosphate. The industry developed with the discovery of new and richer deposits in other parts of the world, until at present the world production of superphosphate greatly exceeds that of all other phosphatic materials combined.

The manufacture of superphosphate in the United States began at Baltimore about 1850.¹ This fertilizer material soon became and still continues to be the basis of the fertilizer industry in this country, amounting to upwards of 50 per cent of the total fertilizer consumption.

The manufacture of superphosphate is a comparatively simple process and consists essentially in treating the ground rock with sufficient sulfuric acid to convert two-thirds of the calcium present into calcium sulfate, leaving the remaining one-third combined with the phosphoric acid as soluble monocalcium phosphate. The principal steps in the process consist in grinding the rock, mixing with a proper proportion of the acid, curing, and drying if necessary.

In the present practice of manufacture the rock is usually ground so that 80-90 per cent will pass a 100-mesh screen. This degree of fineness is easily obtained with present grinding equipment provided the moisture in the rock is within the limits specified for satisfactory grinding. This limit varies with rock from different sources. In the case of Florida rock the moisture content should be reduced below 2 per cent, whereas phosphates from Northern Africa and the Ocean Islands may be ground with a moisture content as high as 5 per cent. The fineness to which the rock is now ground has been considerably increased over that formerly used. This is made possible by the increased efficiency of the present grinding

¹ Twelfth Census of the U. S., 10, Part 4, p. 562.

equipment. Experience has also shown that increased fineness of grinding brings about a saving in the quantity of acid used, increases the speed of the reaction between the acid and the rock and improves the mechanical condition of the resulting product.

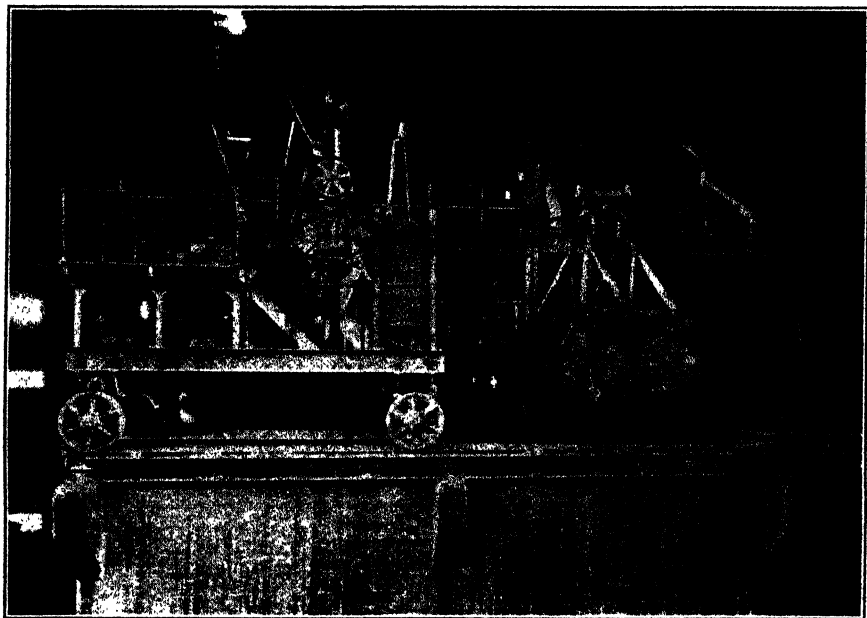


Fig. 2.—Acidulating Machinery and Concrete Silos for the Manufacture of Superphosphate.
Courtesy of the Southern Agricultural Chemical Corporation.

In the mixing operation a definite weight of finely ground rock and a predetermined quantity of 50°-55° Bé. sulfuric acid are usually charged simultaneously into a mechanical mixer of such construction that a thorough mixing of the reacting materials is effected within a period of 1-2 minutes. The resulting mixture is then quickly dumped into one of a series of concrete dens holding 100-400 tons each.

Reaction between the acid and ground rock begins immediately on mixing and continues with evolution of carbon dioxide, steam, silicon fluoride, hydrofluoric acid, and other gases after the mass is discharged into the den. The free water in the acid is absorbed at the same time by the calcium sulfate produced in the reaction to form the hydrated salt

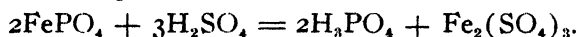
containing 2 molecules of water. This causes the slurry-like mixture discharged into the den to thicken quickly and ultimately set to a comparatively dry, pulverulent product. The setting process is allowed to continue for an indefinite period ranging from 1 to 16 hours or more, when the material is removed, disintegrated and piled, preferably in a well-ventilated building, to cure for a period of two weeks or more. The cured material is finely pulverized and screened when required for shipment or for use in fertilizer mixtures.

The quantity of acid required for a given weight of rock varies with the nature and proportion of the impurities present. The more common of the acid-consuming constituents occurring in phosphates and the acid required per 100 parts of each are as follows:

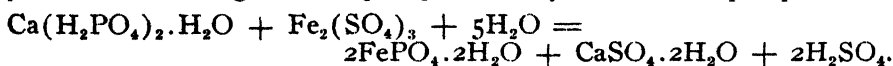
Constituent	Parts of sulfuric acid required per 100 parts of constituent	
	H ₂ SO ₄	52° Bé. acid
Tricalcium phosphate	63.2	97.0
Calcium carbonate	98.0	150.4
Calcium fluoride	125.6	192.8
Alumina	287.7	411.6
Ferric oxide	184.1	282.6

A small proportion of calcium carbonate in the rock may be beneficial because it evolves carbon dioxide and thus produces a lighter, more porous and more friable product. An excess of this constituent, however, is wasteful of sulfuric acid and therefore undesirable. Iron and alumina are not only wasteful of acid but their presence lowers the value of the superphosphate by decreasing the solubility of the finished product and impairing its mechanical properties. They are, therefore, the most objectionable impurities occurring in phosphate rock intended for use in superphosphate manufacture.

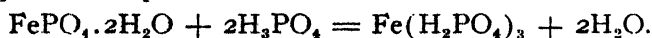
The reaction that takes place between the sulfuric acid and iron phosphate in the rock is represented as follows:



If the iron oxide in the rock is in excess of 2 per cent, a reaction will take place in turn between the ferric sulfate and the monocalcium phosphate present to form a gelatinous precipitate of hydrated ferric phosphate:



The hydrated ferric phosphate reacts with free phosphoric acid to form the more soluble acid salt, and its solubility therefore increases with the free phosphoric acid present:

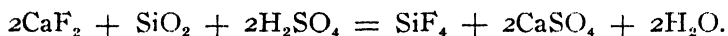


Its solubility, on the other hand, is decreased by any treatment which brings about a dehydration of the compound. This may result from overheating in the den or reaction with anhydrous calcium sulfate:

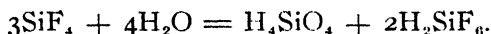


The state of equilibrium that is finally established between these various reactions depends on the conditions of manufacture and the proportion of iron present. The reactions involved in the case of aluminum are similar to those described for iron.

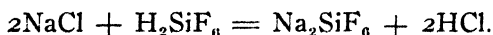
The calcium fluoride in the rock is decomposed by the sulfuric acid to evolve hydrofluoric acid, but the latter reacts with the silica present to form silicon fluoride. The reaction may be represented as follows:



According to Jacob and Reynolds¹ the fluorine evolved amounts to about 25 per cent of the total present. The evolved gases are usually absorbed in a spraying chamber, and the solution is allowed to run to waste. The silicon fluoride in the gas is decomposed by the water sprayed into the chamber to form silicic acid and fluosilicic acid.



In a few of the larger plants the solution is allowed to flow through vats to permit the deposition of the silicic acid and the overflow from the vats is recirculated through the spraying chamber until the solution reaches the proper concentration (6.0-6.7° Bé.) of fluosilicic acid. The solution is then passed through sand filters to separate the silicic acid and the filtrate is treated with a sodium chloride solution to precipitate sodium fluosilicate according to the equation:



This is filtered off, dried and ground for use as an insecticide, an acid rinse in laundries, and for other purposes. In 1925 the production of sodium fluosilicate in the United States from this source was 2,768,000 pounds.

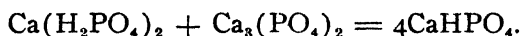
The solution of fluosilicic acid is also used in the preparation of magnesium and zinc fluosilicates by treating with magnesia or zinc oxide and concentrating to crystallize out the respective salts.

Concentrated sulfuric and phosphoric acids are highly hygroscopic materials, and any excess of either constituent gives a sticky product of poor

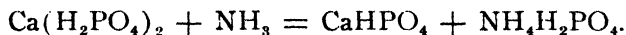
¹ *J. Assoc. Official Agr. Chem.*, **11**, 237 (1928).

mechanical condition. In order to guard against this possibility, somewhat less than the theoretical quantity of acid is used in order to insure a dry, friable product. As a rule best results are obtained when 90-97 parts of 52° Bé. sulfuric acid are used per 100 parts of rock, the acid being increased with increase in iron and aluminum content.

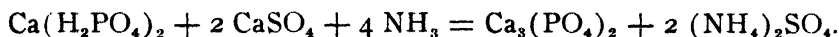
Any change in a superphosphate that results in a decrease in the solubility of the phosphoric acid is spoken of as "reversion." Thus a change from a water-soluble to the citrate-soluble form may result from reaction between the monocalcium phosphate and undecomposed tricalcium phosphate in the superphosphate to form dicalcium phosphate:



The reactions in which iron and aluminum are involved may bring about a reversion of the phosphoric acid to the citrate-insoluble form. A second type of reversion to citrate-insoluble phosphoric acid occurs when superphosphate is treated with a greater quantity of ammonia or other alkaline material than is necessary to form dicalcium phosphate. The actual quantity of ammonia required to form the dicalcium phosphate varies with the free acid present but it is usually about 2 per cent of the superphosphate or approximately one mol equivalent of the monocalcium phosphate present, as indicated by the following equation:



As more ammonia is added a greater or less proportion of the dicalcium phosphate is changed to tricalcium phosphate with formation of more ammonium phosphate. The latter in turn reacts in the presence of ammonia with the gypsum in the superphosphate to form ammonium sulfate and more dicalcium phosphate with continuous progression of the reactions as the treatment with ammonia is continued. The combined reactions may be represented as follows:



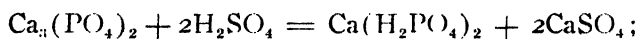
The ammonia content of a superphosphate in which these reactions have gone to completion will range between 8 and 9 per cent. Superphosphate which consists of a mixture of monocalcium phosphate and calcium sulfate can therefore permanently absorb more ammonia in proportion to the phosphoric acid present than a material such as double superphosphate which consists largely of monocalcium phosphate.

If the ammonia added to a superphosphate does not exceed 2.0 per cent by weight the reaction does not proceed beyond the formation of the di-

calcium phosphate and little or no increase in citrate-insoluble phosphate takes place. This method of incorporating nitrogen in a superphosphate is a recent development in the fertilizer industry. The product is known as an ammoniated superphosphate.

DOUBLE SUPERPHOSPHATE

The product formed by treating phosphate rock with phosphoric acid instead of sulfuric acid is variously known as double, triple or treble superphosphate. It differs from superphosphate in that the calcium originally present in the rock is practically all changed into monocalcium phosphate, whereas in superphosphate not more than one-third of the calcium is combined as the monophosphate, the remaining being present as calcium sulfate. The main reactions involved in the preparation of the two products may be represented as follows:



The procedure followed in the manufacture of double superphosphate is much the same as that described for superphosphate. The grade of rock ordinarily selected for the purpose contains 68-70 per cent of tricalcium phosphate, and the grinding treatment to which it is subjected is much the same for either process. The phosphoric acid used in treating the rock has a gravity of 50°-52° Bé. at ordinary temperatures and contains 55-60 per cent H_3PO_4 . This is mixed with the rock at a temperature of about 140° F. in the proportion of 1000 parts of acid to about 550 parts of rock. In making the mix, a little of the ground rock is first run into the mechanical mixer, about one-half of the quantity of acid required is added and the remainder of the rock and acid is then run in simultaneously. The reacting materials are mixed for two minutes or more and then dumped into a rectangular concrete den, open at the top. The mixed product quickly sets to a solid mass and is allowed to remain in the den for 1-6 hours. It is then transferred to suitable piles outside the den and allowed to cure for a period of 10-30 days.

The product prepared in this way is similar to that obtained on treating phosphate rock with sulfuric acid, except that the calcium sulfate in the latter product is replaced with monocalcium phosphate. Calcium sulfate has the property of combining with two molecules of water to form gypsum, while monocalcium phosphate, having almost twice the molecular weight, combines with only one molecule of water. The self-drying ca-

capacity of double superphosphate is consequently much less than that of ordinary superphosphate and the cured product must therefore be dried by artificial means. This is done by passing the moist material through a rotary kiln heated to a maximum kiln temperature of 400° - 500° F. The dry product containing 3-4 per cent moisture is finely crushed, screened and bagged for shipment.

The phosphoric acid (P_2O_5) in double superphosphate, as now manufactured, varies from 40 to 50 per cent as compared with 16-20 per cent in superphosphate. By using mixtures of sulfuric and phosphoric acid in different proportions, it is possible to prepare superphosphates of any desired concentration between the limits given for the ordinary and the double superphosphates. There is therefore no sharp dividing line between superphosphate and double superphosphate.

Table IX gives the composition of representative samples of superphosphate and of double superphosphate.

TABLE IX.—COMPOSITION OF REPRESENTATIVE SAMPLES OF SUPERPHOSPHATE AND DOUBLE SUPERPHOSPHATE.

Constituent	Superphosphate from Florida pebble rock	Double super- phosphate from Western rock
	Per cent	Per cent
Moisture	4.87	2.75
Combined and hydrated water	12.10	
Organic matter	0.53	
Total phosphoric acid, P_2O_5	17.96	48.90
Citrate-insoluble phosphoric acid, P_2O_5	0.62	2.68
Water-soluble phosphoric acid, P_2O_5	16.34	41.40
Available phosphoric acid, P_2O_5	17.34	46.22
Lime, CaO	25.86	20.80
Magnesia, MgO	0.58	0.25
Ferric oxide, Fe_2O_3	0.82	0.97
Alumina, Al_2O_3	1.23	1.26
Potash, K_2O	0.16	0.47
Soda, Na_2O	0.35	1.59
Copper oxide, CuO		0.20
Sulfuric acid, SO_3	29.34	3.75
Fluorine, F	1.53	0.78
Chromic oxide, Cr_2O_3		0.09
Vanadium pentoxide, V_2O_5		0.52
Arsenic trioxide, As_2O_3		0.14
Silica, SiO_2	4.53	1.40

PRECIPITATED PHOSPHATES

Numerous acidulating processes that make use of acids other than sulfuric or phosphoric have been proposed for treating phosphate rock. The acids most commonly used in these methods for increasing the availability of phosphates are hydrochloric, nitric, sulfurous and hydrofluoric. With

one exception none of these processes has yet been developed beyond the experimental stage owing to the relatively high cost of the acid or to the unsatisfactory properties of the finished product. The process which has received most attention and which is now being applied commercially makes use of hydrochloric acid as a solvent agent. In this process the phosphate rock is dissolved in hydrochloric acid, and the resultant solution is neutralized with milk of lime to precipitate the phosphoric acid as dicalcium phosphate. The precipitated phosphate is washed to remove calcium chloride and dried in a rotary kiln. The product formed in this way is a light, finely divided material of good mechanical condition, and it is soluble in ammonium citrate solution.

CALCINED PHOSPHATES

The general procedure for preparing calcined phosphates consists in heating phosphate rock with one or more reagents for the purpose of decomposing the rock or so altering its physical structure that the product will conform with official tests for availability. The reagents most commonly used in these processes are the carbonates, sulfates, chlorides, and silicates of sodium and potassium. The calcined phosphates differ from superphosphate in being neutral or alkaline in reaction and in being almost, or entirely, insoluble in water. Their solubility according to the ammonium citrate or citric acid test varies with the product and the condition of manufacture.

The most extensively used calcined phosphate is a German product known as Rhenania phosphate. The process used for the preparation of this product consists in calcining an intimate mixture of phosphate rock, limestone and a potassium silicate known as phonolite in a rotary kiln at a temperature of 1200°-1300° C. The clinker discharged from the kiln is finely ground and sold as a potash-phosphate fertilizer.

In the Kreiss process (U. S. Patent 1,413,168) a slurry of Florida pebble phosphate in a solution of potassium carbonate is fed into a rotary kiln in which the mixture is first dried and then ignited to a maximum kiln temperature of 1000°-1400° C. The clinker discharged from the furnace is ground to 60 mesh and sold like Rhenania phosphate as a potash-phosphate fertilizer. The potash and phosphoric acid are only slightly soluble in water and the solubility of the phosphoric acid in ammonium citrate solution varies greatly in different samples. A considerable tonnage of this material has been produced in this country, but the process has not been developed to yield a product of uniform composition.

PHOSPHORIC ACIDS

Phosphorus with hydrogen and oxygen forms eight known acids, but only three of these are likely to occur in the free state or as compounds in phosphatic fertilizers. These three acids, known as meta-, pyro- and ortho-phosphoric acids, are formed when phosphorus pentoxide reacts with water.

METAPHOSPHORIC ACID (HPO_3)_n

The ordinary metaphosphoric acid, or glacial phosphoric acid, is a transparent, non-crystalline, vitreous solid, which rapidly absorbs moisture from the air and in solution combines with water to form orthophosphoric acid. The rate of change into the ortho acid increases with rise in temperature and with the concentration of the solution. Sabatier¹ found that complete conversion of a 0.5 *N* solution to the ortho form required 150 days at 0° C.; 5 days at 31° C., and less than an hour at 95° C. Mineral acids accelerate the change, while weak organic acids retard the speed of conversion. The usual method of preparing the acid consists in adding the proper proportion of water to phosphorus pentoxide or in calcining orthophosphoric acid at 300° C. The product prepared by either of these methods is a mixture of a series of polymerized forms of metaphosphoric acid, known as monometaphosphoric acid, dimetaphosphoric acid, etc., each of which has a molecular formula that is a multiple of the first of the series. The first acid in the series is monobasic, and the remainder are polybasic.

PYROPHOSPHORIC ACID ($\text{H}_2\text{P}_2\text{O}_7$)

Pyrophosphoric acid is the second of a series of acids having the general formula $m\text{H}_3\text{PO}_4 - (m - 1)\text{H}_2\text{O}$. When $m = 1$, the general formula becomes that of orthophosphoric acid, the first in the series. The formulas of the remaining acids in the series are multiples of that of orthophosphoric acid less one or more molecules of water. Pyrophosphoric acid (diphosphoric acid) may be prepared by heating equal molecular proportions of ortho and metaphosphoric acids at 100° C., or by adding lead acetate to a solution of an alkali pyrophosphate and decomposing the precipitated lead pyrophosphate with hydrogen sulfide. The acid is tetrabasic and theoretically should form four series of salts. As usually prepared, it is a sirupy liquid, but it may be crystallized, when adjusted to the proper concentration, by seeding or by prolonged action of cold to form an-

¹ *Compt. rend.*, **106**, 63 (1888); **108**, 738, 804 (1889).

hydrous crystals melting at 61° C. It also forms hydrated crystals ($\text{H}_4\text{P}_2\text{O}_7 \cdot 1\frac{1}{2}\text{H}_2\text{O}$), which melt at about 26° C.

Pyrophosphoric acid is similar to the meta acids in that it slowly changes into the ortho acid at ordinary temperatures. The rate of change depends upon the concentration of the hydron in solution and therefore increases with increase in the concentration of the solution or with the addition of strong mineral acids. It also increases with the temperature to a maximum in the neighborhood of 100° C. and then decreases. Abbott¹ found that the hydration of the 0.05 *N* solution was 75 per cent complete in 27 minutes and that the rate of hydration was 10.6 times as great at 100° C. as at 75° , and $(10.6)^3$ times as great at 75° as at 0° . Neither meta nor pyrophosphoric acid gives a precipitate with ammonium phosphomolybdate, and if this reagent is to be used in determining total phosphoric acid in a sample containing either of these acids, it is necessary to acidify with nitric or other mineral acid and boil for about 20 or 30 minutes.

ORTHOPHOSPHORIC ACID (H_3PO_4)

Orthophosphoric acid differs from the meta and pyro acids in being stable in contact with water at ordinary temperatures. Since this is also true of the salts formed from the ortho acids with non-volatile bases, the orthophosphates are the only salts of phosphoric acid that occur in nature.

Orthophosphoric acid is the most important of the numerous acids which phosphorus forms with hydrogen and oxygen. It has a wide application in the arts and industries, but its greatest use is in the production of phosphatic fertilizers.

Anhydrous phosphoric acid is a transparent crystalline solid melting at 42.35° C. As usually prepared for use in the laboratory it is a colorless, sirupy liquid having a specific gravity of 1.71 and containing 85 per cent of orthophosphoric acid. The crystalline acid can be easily prepared by maintaining the sirupy liquid in an open vessel at about 95° C. until it reaches a specific gravity of approximately 1.85 at 25° C., cooling below 40° C., inoculating with a crystal of the anhydrous acid, allowing to stand until crystallization is complete and then separating the crystals from the molten liquor by centrifuging in a porcelain-lined centrifuge. The crystals may be dried over phosphorus pentoxide in a closed desiccator. The crystallization may be repeated when desired by melting the crystals at a temperature of about 50° C., adding sufficient water to bring to a specific gravity of 1.85 at 25° C., cooling below 40° C., and reinoculating as be-

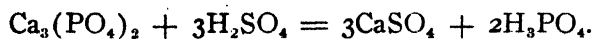
¹ *J. Am. Chem. Soc.*, **31**, 763 (1909).

fore. This is the simplest and most effective method of preparing orthophosphoric acid of a high degree of purity.

Orthophosphoric acid also crystallizes in the form of a hydrate having the composition $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$. The hydrated crystals melt at 29.32°C . Their low melting point and marked tendency to cake make their use inconvenient in the purification of phosphoric acid. The solubility curves of hydrated and anhydrous orthophosphoric acid have been determined by Ross and Jones.¹

Two methods are now in use for the commercial preparation of orthophosphoric acid. They are known as the sulfuric and volatilization methods. Phosphate rock is now the only source of phosphoric acid in the volatilization process, as well as the most commonly used source in the sulfuric acid method. Bones have been widely used in the sulfuric acid method, but they are now being replaced by the cheaper phosphate rock.

In the sulfuric acid process of producing phosphoric acid the rock is first dried and ground as in the manufacture of superphosphate. If the organic content is relatively high, as in most Western phosphates, the rock is also calcined at 1300°F . to eliminate most of the organic matter. Two methods are in use for the extraction of phosphoric acid from the rock. In the older procedure the dried, ground rock is treated with 30°Bé . sulfuric acid and the resulting product is then passed through a series of filter presses to remove the undissolved and precipitated material. In the most modern plants, however, the Dorr system of counter-current extraction is used. The initial steps here differ somewhat in different plants but the general procedure consists in first treating the ground rock in an agitating tank with the overflow of dilute phosphoric acid from the No. 2 thickener and then with a predetermined quantity of 60°Bé . sulfuric acid. The reaction between the acid and the calcium phosphate of the rock, its principal component, is as follows:



The slurry from the first agitating tank overflows successively into a second and third agitating tank, taking 18-24 hours to go through the three tanks. The temperature in the first agitator reaches about 66°C . while that of the discharge from the third is about 55° . From the third agitator the slurry passes into the first of a series of six Dorr thickeners, the purpose of which is to bring about a separation of the phosphoric acid from the insoluble material or sludge by continued counter-current decantation.

¹ *J. Am. Chem. Soc.*, **47**, 2165 (1925).

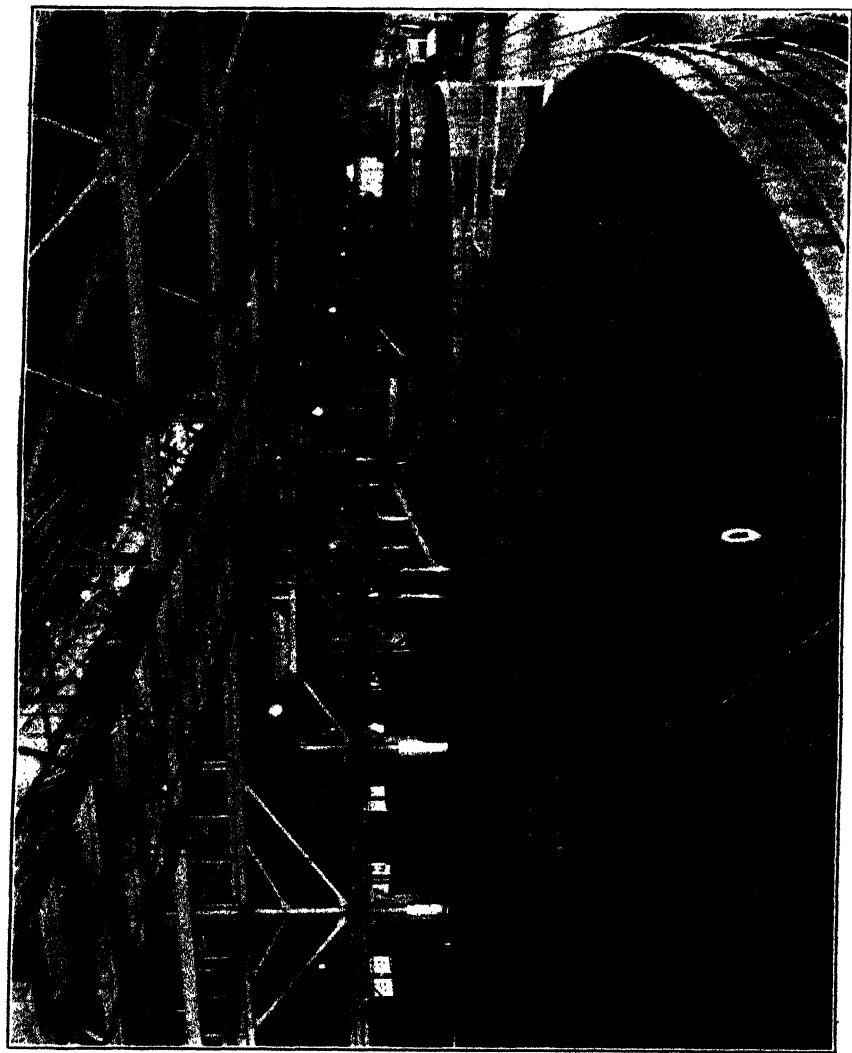
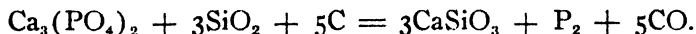


Fig. 3.—Dorr Thickeners for the Manufacture of Phosphoric Acid.
Courtesy of the Anaconda Copper Mining Company.

The clear solution that overflows from the first of the thickeners has the maximum concentration that it is possible to obtain by the sulfuric acid process, namely 25-28 per cent orthophosphoric acid. The gypsum sludge that settles out in the thickeners is successively pumped from one to the next and is washed by a solution of increasing concentration, which overflows from thickener to thickener in an opposite direction. The overflow from No. 2 thickener containing about 15 per cent of H_3PO_4 is returned to the system for the preliminary treatment of the phosphate rock as previously mentioned. The sludge discharged from No. 6 thickener is filtered on an Oliver filter and the filtrate, diluted with the proper amount of water, is returned to No. 6 thickener as a source of supply of the washing solution. The filtered sludge is either thrown away or used as a source of gypsum in the manufacture of building block.

In the volatilization or pyrolytic method of producing phosphoric acid a mixture of 30 parts of phosphate rock, 10-15 parts of sand, and about 5 parts of coke is charged into an electric or fuel-fired furnace and heated in a reducing atmosphere to a temperature of 1500° - 1700° C. Under these conditions the phosphorus in the rock is volatilized in the elementary state, while the residual mass is reduced to a molten slag which is tapped at intervals from the furnace. The reaction taking place varies somewhat with the ratio of lime to silica in the charge. When these are present in equimolecular proportions the reaction may be represented as follows:



If the furnace is so constructed that air is admitted at the top, the phosphorus and carbon monoxide are oxidized as they escape from the charge to phosphorus pentoxide and carbon dioxide. In the electric furnace process the gases are withdrawn from the furnace by suction and are passed in turn through a series of humidifiers and finally through an electric precipitator. The humidifier serves the double purpose of cooling the gases and of hydrating the phosphorus pentoxide to phosphoric acid. As the gases pass through the precipitator minute droplets of liquid acid are deposited by electrostatic action on the walls of the apparatus to form a concentrated solution of phosphoric acid, while the gaseous products pass through unchanged.

The hydration of phosphorus pentoxide to phosphoric acid is a comparatively slow reaction at ordinary temperatures, but under the conditions prevailing in the volatilization process the reaction becomes very rapid, and complete conversion to orthophosphoric acid takes place during

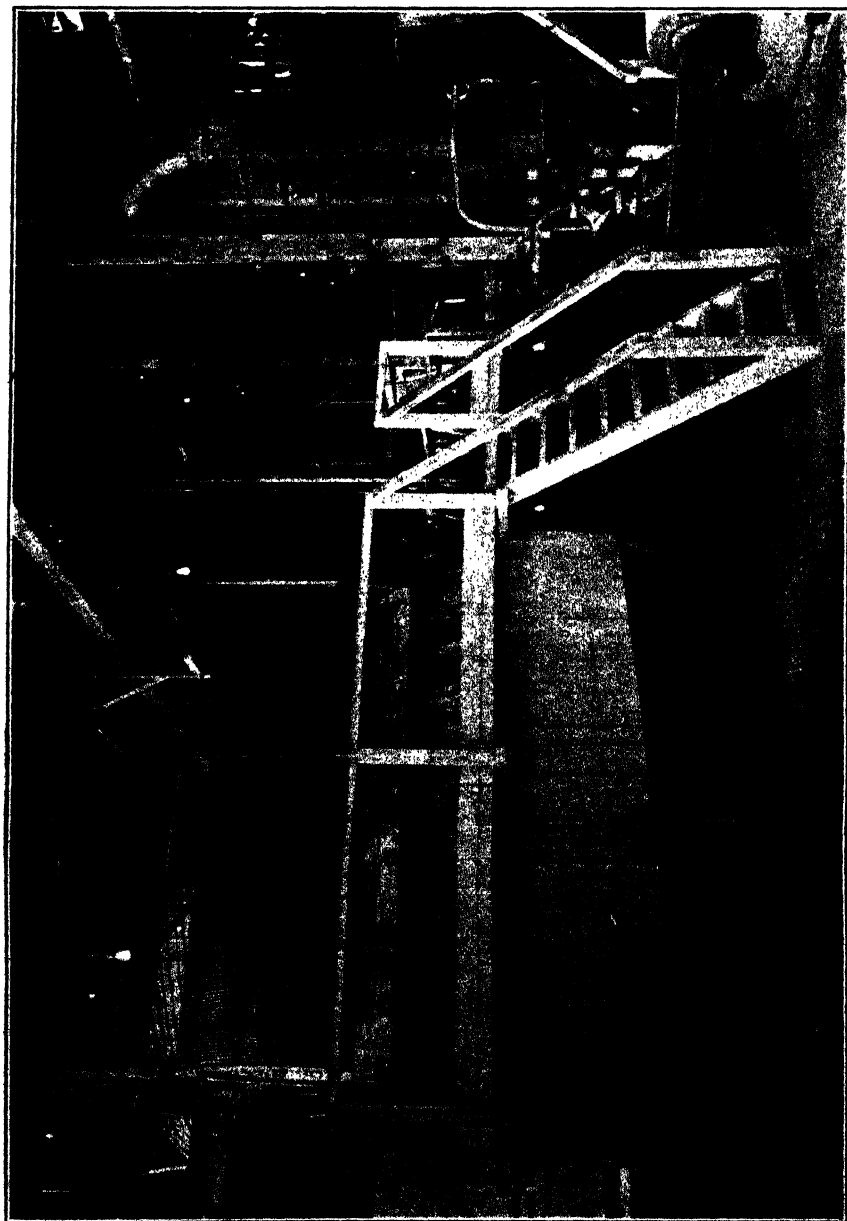


Fig. 4.—Oliver Filter for the Separation of Gypsum Sludge from Phosphoric Acid.
Courtesy of the Anaconda Copper Mining Company.

the brief interval required for the gases to pass from the furnace to the precipitator. The commercial acid usually recovered by this process has a concentration of about 80 per cent orthophosphoric acid. By increasing the temperature at which precipitation is made, however, it is possible to



Fig. 5.—Equipment for the Recovery and Treatment of Volatilized Phosphoric Acid.

Courtesy of the Swann Corporation.

increase the concentration of the acid so that the recovered product solidifies on cooling to a solid mass of phosphoric acid crystals.

Volatilized phosphoric acid is thus not only more concentrated than that prepared by the sulfuric acid method, but the quality of the acid is superior, because it contains a smaller percentage of impurities. This is shown in Table X, which gives the composition of several grades of phosphoric acid.

ALKALI PHOSPHATES

ALKALI METAPHOSPHATES

Since the first member of the series of metaphosphoric acids is monobasic and the other members are polybasic, a large number of alkali meta-

TABLE X.—COMPOSITION OF SOME COMMERCIAL PHOSPHORIC ACIDS

Phosphoric acid*	Sp. gr. at 25° C.	Concentration, H ₃ PO ₄	Constituents present on basis of 50 per cent concentration H ₂ SO ₄																						
			Na		K		Ca		Fe		Al		Mn		HCl		HF		Pb		As ₂ O ₃		Total		
			Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	P. p. m.	P. p. m.	P. p. m.	Per cent			
A	1.4606	53.47	0.20	trace	0.14	1.21	0.66	0.126	0.47	0.012	0.20	3.02													
A	1.2371	27.60	0.76	0.18	1.20	1.88	1.22	0.149	0.65	0.027	1.54	7.36													
B	1.5428	60.99	0.13	0.04	0.04	0.18	0.27	0.004	0.27	0.013	0.10	4	1.0	1.13											
C	1.4123	55.20	0.41	0.12	trace	0.19	0.10	0.155	0.46	0.044	0.05	7	0.75	1.53											
C	1.4221	55.12	0.35	trace	0.16	0.34	0.23	0.348	0.13	0.035	0.11	4	1.0	1.70											
C	1.3261	39.40	0.06	0.03	0.11	1.00	1.25	0.184	1.25	0.012	0.96	14	1.0	4.89											
D	1.3865	52.27	0.16	trace	0.20	0.50	0.11	0.014	0.12	0.003	0.04	0	2.5	1.45											
D	1.2309	32.15	0.53	trace	1.36	0.84	0.19	0.021	0.28	0.023	0.14	9	1.0	3.39											
E	1.3955	56.89	0.10	0.16	none	0.08	0.04	0.005	0.09	0.000	0.02	12	1.0	0.50											
E	1.6310	79.50	0.12	0.18	trace	0.17	0.06	0.004	0.07	0.000	0.01	8	0.5	0.61											

*A. Crude acid from phosphate rock—sulfuric acid method.

B. Crude acid from phosphate rock—volatilization process and recovered by absorption in water.

C. Refined acid from phosphate rock—sulfuric acid method.

D. Refined acid from bones—sulfuric acid method.

E. Refined acid from phosphate rock—volatilization process.

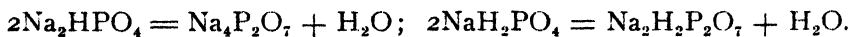
phosphates is theoretically possible, but their preparation in a pure state is very difficult owing to their instability and to the fact that they do not readily crystallize. One of these polymetaphosphates, known as ammonium-potassium-pentametaphosphate, has the formula $\text{NH}_4\text{K}_4\text{P}_5\text{O}_{15} \cdot 6\text{H}_2\text{O}$. Although this compound has no commercial application at present it is of interest because it affords an example of a definite chemical compound that contains all three fertilizing elements.

The alkali salts of the metaphosphoric acids may be prepared by neutralizing the aqueous solution of the acid with the corresponding alkali hydroxide. Potassium monometaphosphate (KPO_3) may also be formed by heating monopotassium orthophosphate at a low red heat until the loss in weight of the previously dried salt amounts to 12.23 per cent. Potassium metaphosphate is one of the least soluble of the potash salts. It is also of interest because it contains exactly 100 per cent of fertilizer constituents.

ALKALI PYROPHOSPHATES

Pyrophosphoric acid is a tetrabasic acid and is theoretically capable of forming four alkali salts according as one or more of the hydrogen ions of the acid is replaced with an alkali metal. The quaternary or normal pyrophosphates and the secondary phosphates are well-known salts, but there is some doubt whether the ternary and primary salts have ever been prepared in the solid state. The pyrophosphates of the alkali metals are all soluble in water, but those of the other metals are insoluble. The best known of the insoluble pyrophosphates is the normal magnesium pyrophosphate. This is formed as a snow-white residue on igniting the ammonium magnesium phosphate obtained in the molybdate-magnesium method of determining phosphoric acid.

The normal sodium and potassium pyrophosphates may be easily prepared by heating the corresponding di-salt of orthophosphoric acid at a temperature of $240\text{--}250^\circ\text{C}$. for 8-12 hours. A similar treatment of the monoorthophosphate yields a secondary pyrophosphate. These reactions in the case of the sodium salt are represented as follows:



The secondary alkali phosphates, including the ammonium salts, may also be prepared by adding the corresponding alkali hydroxide to a solution of pyrophosphoric acid until it reacts neutral to methyl orange.

The normal alkali pyrophosphates are alkaline in reaction, while the secondary pyrophosphates are acid to phenolphthalein but neutral to methyl

orange. The secondary alkali pyrophosphates may be kept indefinitely in a dry place without change, but when they are boiled in acid solution they quickly change to the orthophosphates.

ALKALI ORTHOPHOSPHATES

Orthophosphoric acid, being a tribasic acid, reacts with the alkalies to form three orthophosphates known as the mono-, di-, and tri-compounds. The monoalkali orthophosphates are slightly acid in reaction, the di-phosphates slightly alkaline, and the triphosphates strongly alkaline.

The alkali orthophosphates have wide application in the industry, but the mono- and diammonium orthophosphates are the only alkali phosphates used at present in the manufacture of commercial fertilizers. The mono-ammonium orthophosphate is stable at all temperatures up to about 125° C. The di-salt quickly decomposes at this temperature, but it is stable at ordinary temperatures when in the dry state. If the salt becomes moist some loss of ammonia occurs at ordinary temperatures, but little or no loss takes place in mixtures of this compound with the mono-salt. The stability of diammonium phosphate when stored in a damp place may therefore be increased by mixing it with a quantity of the monoammonium phosphate.

The triammonium phosphate, being strongly alkaline in reaction, is very unstable and rapidly changes into the di-compound with loss of ammonium at room temperatures. The reactions taking place in the decomposition of the tri- to the di-compound, and of the latter to the mono-phosphate, may be represented as follows:



Table XI gives a summary of some of the more characteristic properties of the ammonium orthophosphates. It shows that diammonium phosphate is the most soluble of the three phosphates, and triammonium phosphate the least. The solubility of the triammonium phosphate decreases rapidly with excess of ammonia and amounts to only 0.16 gram per 100 grams of solvent when dissolved in an ammonia solution of 0.90 sp. gr. It is therefore precipitated as a white crystalline salt when sufficient gaseous ammonia or a strong ammonia solution is added to phosphoric acid or to a strong solution of either of the other compounds. It may be obtained in a dry state by passing a stream of ammonia over the material in a closed vessel at 90°-100° C.

TABLE XI.—PROPERTIES OF THE AMMONIUM ORTHOPHOSPHATES.

Compound	Crystal form	Solubility at 25° Grams per 100 grams of water	Heat of formation from gaseous NH_3 and solid H_3PO_4 Calories	Ammonia vapor pressure at		pH of 0.1 <i>M</i> solution	Reaction of 0.1 <i>M</i> solution to indicators
				100° C.	125° C.		
Monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$	Tetragonal	40.0	29,000	0.00	0.05	4.4	Alkaline to methyl orange; acid to methyl red
Diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$	Monoclinic	60.5	48,500	5.3	39.0	7.8	Neutral to cresol red
Triammonium phosphate $(\text{NH}_4)_3\text{PO}_4$	Orthorhombic	17.7	58,400	64.3	1177	9.0	Neutral to thymol blue in alkaline range

Ammonia and phosphoric acid are also used as raw materials in the commercial preparation of monoammonium phosphate. In the process now generally used for preparing crude monoammonium phosphate for fertilizer purposes, crude phosphoric acid produced by the sulfuric acid method is rapidly neutralized with ammonia in open vessels to the point where the solution reacts yellow to methyl orange and red to methyl red. The heat of the reaction is sufficient to raise the temperature of the liquid to the boiling point and to bring about some loss of water by evaporation, but the concentration that takes place is not sufficient to saturate the solution at the boiling point. The iron and aluminum phosphates present precipitate out, however, to form a slurry which is difficult to filter. The whole mass is accordingly reduced to dryness by feeding it into a rotary kiln that is maintained at a temperature below 120°C .¹

Two grades of ammonium phosphate for fertilizer purposes are now being marketed under the trade name of Ammophos by the largest commercial producer in this country. The 13-48 grade is guaranteed to contain 13 per cent ammonia (NH_3) and 48 per cent available phosphoric acid (P_2O_5). The ammonia is present almost entirely as monoammonium phosphate, accompanied by a small percentage of ammonium sulfate and such minor constituents as iron and aluminum phosphates, which originally occurred as impurities in the phosphoric acid. The 20-20 grade differs from the 13-48 grade in that it contains a higher percentage of ammonium sulfate. It is prepared by adding sulfuric acid to the recovered phosphoric acid. A mixture of the phosphate and sulfate of ammonium is therefore obtained when the mixed acids are neutralized with ammonia. This grade of Ammophos contains a lower proportion of impurities than the 13-48 grade due to the greater relative purity of commercial sulfuric acid as compared with crude phosphoric acid. Ammophos is sold in 17 countries throughout the world. The production at present amounts to 200,000 tons per annum.

In the preparation of technical monoammonium phosphate, use is made of a refined acid, such as that produced by the volatilization method. This acid, with the equivalent amount of ammonia, is added to the mother liquor from a previous batch until the solution becomes nearly saturated at the temperature to which it is raised by the heat of the reaction. The solution is then allowed to cool in a crystallizer of the Walker type, and the crystallized salt is recovered by centrifuging.

¹ Ross, Merz and Jacob, *Ind. Eng. Chem.*, **21**, 286 (1929).

A similar process is used in the preparation of diammonium phosphate.¹ The acid is first added to a solution of the salt saturated at room temperature until it changes the color of bromcresol purple, or until the phosphoric acid content of the solution is increased by about one-third. Gaseous ammonia and phosphoric acid are then added simultaneously in the proportion of 1.5 mols of the former to 1 of the latter, and at such a rate that the temperature does not exceed 80°-90° C. The addition of the ammonia and phosphoric acid is continued until the phosphate content of the solution is approximately doubled. The solution is then cooled to room temperature, and ammonia is added until the solution reacts neutral to cresol red. The coarse monoclinic crystals of diammonium phosphate that separate from solution under these conditions are centrifuged and then dried at 60° C., and the mother liquor is added to the next batch for use again in the process.

The mono- and disodium phosphates are prepared by treating a strong solution of soda ash with sufficient phosphoric acid to give a saturated solution of the desired salt, and then cooling to crystallize out the salt from the solution. The third hydrogen atom of phosphoric acid cannot be replaced by the sodium in sodium carbonate, and the hydroxide of soda must therefore be used for this purpose in place of the carbonate. Trisodium phosphate has a wide application as a water softener as well as for other purposes, and its production exceeds that of any other sodium phosphate. The usual process of preparation consists in adding a strong solution of caustic soda to a clear solution of disodium phosphate, filtering, cooling the filtrate to crystallize out the hydrated salt containing 12 mols of water, centrifuging, and drying below 70° C.

The methods used in the preparation of the potassium phosphates are similar to those outlined for the corresponding sodium phosphates. The di- and tripotassium phosphates do not crystallize readily and are of little commercial importance. The monopotassium phosphate, on the other hand, resembles the monoammonium phosphate, in that it crystallizes readily without water of hydration and is not hygroscopic. Its chemical and physical properties make it admirably suited for use in fertilizers, but the cost of manufacture has so far interfered with its commercial production for this purpose. It may be prepared in mixture with ammonium phosphate by digesting potassium chloride in a shale brick chamber with an excess of concentrated phosphoric acid at a temperature of about 250° C. Hydrochloric acid is evolved in the process and may be recovered as a

¹ Griessbach, Balz and Rossler, U. S. Patent 1,670,504 (1928).

by-product. The liquid remaining at the end of the reaction consists of a concentrated solution of potassium phosphate in phosphoric acid. On neutralizing the latter with ammonia, the whole mass is precipitated as an isomorphic mixture of monopotassium and monoammonium phosphates.¹

ANALYTICAL PROCESSES

The determination of phosphoric acid has received more attention on the part of analysts than any other determination in quantitative analysis owing to its important commercial applications and to the inaccuracy and tediousness of many of the earlier methods. Many changes are still being made by different analysts in order to increase the accuracy and rapidity of their work. The result has been an extraordinarily large number of different methods and a large number of variations of the methods that are most often used.

For convenience of treatment, these methods are divided into the two main groups of gravimetric and volumetric methods, while each of these groups is divided in turn into two subgroups according as the phosphoric acid is or is not first separated as ammonium phosphomolybdate. The methods which do not involve precipitation with ammonium molybdate are further classified into a number of groups according to the reagent used in bringing about the final separation of the phosphoric acid. The methods involving precipitation with ammonium molybdate are also subdivided into a number of groups according to the treatment to which the ammonium phosphomolybdate is subjected. The groups into which the gravimetric methods are divided are as follows:

CLASSIFICATION OF GRAVIMETRIC METHODS

Methods not involving molybdate precipitation

Uranium
Silver
Bismuth
Lead
Calcium
Aluminum
Copper
Tin
Magnesium

Methods involving molybdate precipitation

Direct weighing
Molybdate-magnesium

¹ Ross, *Trans. Am. Electrochem. Soc.*, **48**, 299 (1925).

For a classification of the volumetric methods see page 151.

A detailed description is given of those methods which have been or are still being generally used in the analysis of phosphatic materials, and a history of their development is outlined in some detail to show the modifications that have been made in each method since it was originally proposed. A brief outline is also given of certain methods which are of historic interest but which have never been adopted in commercial laboratories.

The principal methods that have been proposed for the determination of total phosphoric acid are applicable to the analysis of all phosphatic materials with variations only in the manner in which the sample is brought into solution. A historical review is accordingly given of the development of the various procedures for preparing solutions of samples of different phosphatic materials under the following headings: (1) Total phosphoric acid, (2) water-soluble phosphoric acid, (3) citrate-soluble phosphoric acid, and (4) citric acid-soluble phosphoric acid.

When the analyst has no preferred method for the analysis of any given material he should refer to the official methods (pp. 187-212) that have been adopted by different organizations throughout the world for the analysis of phosphatic materials and select the method applicable to the material in hand.

PREPARATION OF SOLUTION

TOTAL PHOSPHORIC ACID

The official methods of the Association of Official Agricultural Chemists now include four methods for bringing fertilizers into solution for a determination of their total phosphoric acid content, each specifying the kind of materials for which it is best suited. Prior to 1924 there were seven such methods, only one of which was specifically recommended, namely, that for fertilizers containing much iron and aluminum. A brief historical account is given here of the circumstances under which each of these methods was adopted.

Ignition with Magnesium Nitrate and Solution in Acid.—The original method of the Association for obtaining a total phosphoric acid solution as given in the Proceedings of the First Annual Meeting held at Philadelphia in 1884, directed the addition of 4-7 cc. of a nearly saturated

¹ *Methods of Analysis, A. O. A. C.*

solution of magnesium nitrate to a 2 gram sample, drying, igniting gently, moistening the residue with nitric acid, if necessary, reigniting to destroy all organic matter, adding 15-20 cc. of concentrated hydrochloric acid, digesting at a gentle heat until all phosphates are dissolved, diluting to 200 cc., mixing, passing through a dry filter, and taking an aliquot for the determination.

The magnesium nitrate solution was prepared by dissolving 320 grams of "calcined magnesia" in nitric acid, avoiding an excess of the latter, then adding a little calcined magnesia in excess, boiling, filtering to remove the excess of magnesia, ferric oxide, etc., and bringing to a volume of 2 liters.

This method was supposed to be used on all materials, although many analysts apparently did not apply it to simple rock phosphates or superphosphates.¹ The use of hydrochloric acid rather than nitric acid had been adopted because hydrochloric acid was found to dissolve more readily and quickly, though, with care, nitric acid answered perfectly. Although the presence of chlorides, introduced by the hydrochloric acid, somewhat retarded, it did not prevent the precipitation of ammonium phosphomolybdate. In a comparison of the two solvents the results differed in only a small number of cases, and in these hydrochloric acid invariably gave slightly higher results.

An early objection² to the ignition of the sample with magnesium nitrate was that it required some time and an additional transfer of the material from one vessel to another, involving the possibility of mechanical loss. The committee of the Association on phosphoric acid in 1885 therefore recommended that experiments were desirable to determine whether organic matter could be destroyed or made harmless in the wet way, by fuming nitric acid or other reagents, in the flask in which the subsequent solution of the phosphate was to be made. Gladding pointed out that the results of analyses on superphosphates from phosphorites were practically identical, whether a simple solution in hydrochloric or nitric acid, a fusion with sodium carbonate (with subsequent solution in water and hydrochloric acid), or an ignition with sulfuric acid was employed, and advocated the omission of the use of magnesium nitrate in all such cases where it was known to be unnecessary. As a result of the work done in accordance with these recommendations, the magnesium nitrate ignition method was dropped in 1886, but in 1887 the method was again included

¹ U. S. Dept. Agr. Div. Chem. Bull., 7, 15 (1885).

² *Ibid.*, 14.

as an optional official method.¹ No particular acid was specified at this time for solution of the ignited residue, but in 1891 the use of hydrochloric acid was prescribed for this purpose.²

In 1890³ Burney and Battle recommended that this method be used for all fertilizers containing cottonseed meal or other organic material. Gascoyne reported that it was almost impossible to get the entire amount of phosphoric acid from cottonseed meal with any of the wet processes and that it could only be done by the magnesium nitrate method, but he saw no reason for extending the method to any other substance. Frear also reported it advantageous for cottonseed meal, but opposed its extension to all fertilizers containing any kind of organic matter. In the same year the Association⁴ recommended the use of this method for all fertilizers containing cottonseed meal.

Shiver⁵ reported that, although the magnesium nitrate method gave accurate results, it was not so rapid as the Burney method (see p. 91) and in practice difficulties, such as sputtering, were presented. In addition to the danger of loss by intumescence, other objections were raised against the magnesium nitrate method in 1891, such as the occasional fusing of the mixture to a hard mass which adheres to the sides of the vessel and to the separation of flocculent or gelatinous precipitates containing magnesium and phosphoric acid from the acid solution on boiling. Ignition with magnesium nitrate ceased to be prescribed for fertilizers containing cottonseed meal in 1891; it was merely recommended as an optional official method for such fertilizers and those containing much organic matter. In 1924⁶ the words, "Suitable for organic materials like cottonseed meal alone or in mixtures," were added.

Solution in Hydrochloric Acid with the Addition of Potassium Chlorate.—White⁷ compared (a) digestion of the sample for 30 minutes with 30 cc. of concentrated hydrochloric acid, (b) similar digestion but with the addition at intervals of pinches of finely powdered potassium chlorate (0.5 gram in all), (c) digestion for 30 minutes with 30 cc. of fuming nitric acid, and (d) ignition with magnesium nitrate. He found that the use of potassium chlorate with hydrochloric acid was by far the best method, both in

¹ U. S. Dept. Agr. Div. Chem. Bull., **16**, 140 (1887).

² *Ibid.*, **31**, 180 (1891).

³ *Ibid.*, **28** (1890).

⁴ *Ibid.*, 228.

⁵ *Ibid.*, **31**, 109 (1891).

⁶ *J. Assoc. Official Agr. Chemists*, **8**, 261 (1925).

⁷ U. S. Dept. Agr. Div. Chem. Bull., **12**, 28 (1886).

convenience and results, for analyzing two fertilizers, one of which contained animal matter and the other cottonseed meal. At the same meeting Jenkins also recommended the adoption of this method, which consequently was adopted as official in 1886 in place of the magnesium nitrate method. The method read as follows:

Weigh 2 grams into a flask or beaker; add 30 cc. of concentrated hydrochloric acid; heat and add cautiously and in small quantities at a time about 0.5 gram of finely-powdered potassium chlorate. Digest at a gentle heat until all phosphates are dissolved and all organic matter is destroyed; dilute to 200 cc.; mix; pass through a dry filter; take 50 cc. of filtrate.

Jenkins¹ later found this method to be very unsatisfactory with fertilizers containing castor pomace and its use also met with considerable opposition from others. Meyers¹ reported that he had found it next to impossible to extract all the phosphoric acid by this procedure. In 1887, therefore, with a view to allowing the analyst greater latitude in the manner of treatment of the sample, this method became merely an optional official method, and it has appeared from that time in *Methods of Analysis* as one of the procedures that may be used. Dancy² and Huston³ also gave very unfavorable reports on this method. It was dropped as an official method in 1924.⁴

Solution in Nitric Acid with a Small Quantity of Hydrochloric Acid.—Richards⁵ found that solution in nitric acid without previous ignition of the fertilizer containing organic matter gave results agreeing very closely with the official magnesium nitrate ignition method. Gascoyne⁵ likewise found that solution of 2 grams of a fertilizer in 50 cc. of concentrated nitric acid and a few drops of hydrochloric acid gave as satisfactory results as the magnesium nitrate method. In 1887, this method of solution was adopted, with the two methods already discussed, as an optional treatment prior to the phosphoric acid determination.⁶ The wording of the method as adopted was as follows:

Treat 2 grams of the sample in 30 cc. of concentrated nitric acid and a small quantity of hydrochloric acid. Boil gently until all phosphates are dissolved and all organic matter is destroyed; dilute to 200 cc., mix, and pass through a dry filter paper, and take an aliquot of the filtrate for the phosphoric acid determination.

¹ U. S. Dept. Agr. Div. Chem. Bull., **16**, 40 (1887).

² *Ibid.*, **28**, 161 (1890).

³ *Ibid.*, **31**, 98 (1891).

⁴ J. Assoc. Official Agr. Chem., **3**, 261 (1925).

⁵ U. S. Dept. Agr. Div. Chem. Bull., **12**, 24 (1886).

⁶ *Ibid.*, **16**, 59 (1887).

Burney¹ reported that boiling for many hours was sometimes insufficient treatment to clarify the solution by destruction of the organic matter, so that the method was not always successful. Dancy² found that cottonseed meal is readily and entirely soluble in either nitric acid with a small quantity of hydrochloric acid or in nitric acid alone, but the fact that the solution does not give up its phosphoric acid to molybdate solution made the method entirely inadequate. Apparently certain nitro-organic compounds are formed which prevent the precipitation of the phosphoric acid.

Doolittle³ called attention to the difficulty of interpreting the expression "dissolve in 30 cc. of concentrated nitric acid and a small quantity of hydrochloric acid," and in consequence the 1925 edition of *Methods of Analysis* prescribes the use of 3-5 cc. of strong hydrochloric acid. In 1924⁴ the words, "Suitable for materials containing small quantities of organic matter," were added.

Solution in Concentrated Sulfuric Acid with the Addition of Potassium or Sodium Nitrate.—This method as first described by Burney⁵ consisted in introducing the substance (2 grams) into a Kjeldahl flask, adding 10 cc. of concentrated sulfuric acid, and after gently boiling for a few minutes, adding small pieces of potassium nitrate occasionally and making the boiling more brisk. He stated that oxidation was complete in 20-30 minutes. The nitric acid and other products of distillation condense on the walls of the flask and flow back to the bottom, thus cleansing the sides of the digestion flask. By this method the oxidizing action of the nitric acid is secured at a very high temperature, something like 300° C.

Collaborative work under the auspices of the Association⁶ had confirmed the inadequacy of the methods using concentrated nitric acid with a small quantity of hydrochloric acid, and hydrochloric acid with potassium chlorate for goods containing cottonseed meal and similar materials, such as bran and fish, although the phosphoric acid of blood and bones could be completely precipitated with molybdate when these methods of solution were used.

Shiver⁷ found that Burney's method of digestion with sulfuric acid and potassium nitrate gave results which did not differ by more than 0.15 per

¹ U. S. Dept. Agr. Div. Chem. Bull., **24**, 98 (1890).

² *Ibid.*, **28**, 161 (1890).

³ J. Assoc. Official Agr. Chem., **7**, 197 (1924).

⁴ *Ibid.*, **8**, 262 (1925).

⁵ *Loc. cit.*

⁶ U. S. Dept. Agr. Div. Chem. Bull., **31**, 98, 105 (1891).

⁷ *Loc. cit.*

cent from those obtained by the magnesium nitrate method on fertilizers containing cottonseed meal and that in many cases the results were identical. Accurate results were also obtainable on fertilizers containing fish scrap, dried blood, tankage, bone meal, and other organic materials. The method, however, was not applicable to all substances containing phosphoric acid. It gave, for example, in the case of a high-grade aluminic phosphate, a precipitate of ferric sulfate that separated out and required heating to bring it back into the solution, and it did not give accurate results with highly silicious materials unless precautions were taken to separate the silica; with superphosphates the tendency was to give too high results. The principal objection to this method was the formation of a large quantity of finely divided calcium sulfate, which had a tendency to pass through the pores of the filter. He stated, however, that this could be overcome and recommended the method as one giving quick and accurate results.

Huston, the referee on phosphoric acid, therefore recommended that the Burney method should be included among the official methods of solution for the determination of total phosphoric acid, but that the use of either potassium or sodium nitrate should be permitted. The method was accordingly adopted¹ in 1891 in the following form and recommended as an optional official method for fertilizers containing cottonseed meal or much organic matter.

Boil 2 grams with 20-30 cc. of strong sulfuric acid, adding 2-4 grams of sodium or potassium nitrate at the beginning of the digestion, and a small quantity after the solution has become nearly colorless, or adding the nitrate in small portions from time to time. A Kjeldahl flask graduated to 250 cc. is recommended. After the solution is colorless add 150 cc. of water, boil for a few minutes, cool, and make up to volume.

At the same meeting Huston reported that the crystals which sometimes form in solutions resulting from the treatment of phosphates with sulfuric acid after standing for a day or so contained no phosphoric acid. He also stated that molybdate precipitation is incomplete unless the strongly acid solution be neutralized with ammonia and then slightly acidified with nitric acid and confirmed the claim that low results are obtained with high-grade aluminic phosphate.

In 1924² the words "200 cc. flask" were substituted for "Kjeldahl flask," and there was added "Generally applicable to materials or mixtures con-

¹ U. S. Dept. Agr. Div. Chem. Bull., **31**, 180 (1891).

² *J. Assoc. Official Agr. Chem.*, **8**, 262 (1925).

taining large quantities of organic matter. With cottonseed meals and materials of like nature, it is best to add about 5 cc. of concentrated nitric acid before the addition of the sulfuric acid, and allow to digest, at a gentle heat if necessary, until the violence of the reaction is over, before adding the nitrate."

The sulfuric acid method as thus adopted was also found to give good results in the volumetric, as well as in the gravimetric, determination of phosphoric acid and in 1929 it was recommended¹ as an optional official method for use in the volumetric determination of phosphoric acid in samples high in organic matter.

Solution as in the Kjeldahl or Gunning Method for Nitrogen.—De Roode² first introduced this method, which permits the determination of both phosphoric acid and nitrogen in the same sample. He placed 2.5 grams of the fertilizer in a Kjeldahl digestion flask and proceeded exactly as in the official Kjeldahl method, plain or modified, as described by Scovell,³ for the determination of nitrogen in nitrates. When the contents of the flask had cooled, about 50 cc. of water was added and the mixture was boiled. The flask was cooled in a current of cold water, and its contents were transferred to a 250 cc. measuring flask, made up to the mark with rinsings, mixed and filtered through a dry fluted filter into a dry flask. The phosphoric acid was determined in a 50 cc. aliquot after being nearly neutralized with ammonia.

Huston⁴ found that the method as outlined above gave considerable trouble owing to a precipitate containing manganese and phosphoric acid, which appeared when the solution was neutralized and was not wholly soluble in nitric acid. This accounted for the very high results obtained by the method in the cooperative work of the Association. The trouble was easily corrected by adding to the neutralized solution a small quantity of ferrous ammonium sulfate. He recommended that the method, without the use of the permanganate, be adopted as official. Although De Roode claimed that if a small excess of permanganate were added the color could be made to disappear by boiling for a few minutes and the determination of phosphoric acid was then not interfered with, Frear stated that the use of permanganate could not be relied on. The method was accordingly adopted as official in 1891 in the following form and recom-

¹ *J. Assoc. Official Agr. Chem.*, **13**, 60 (1930).

² U. S. Dept. Agr. Div. Chem. Bull., **31**, 98, 104 (1891).

³ *Ibid.*, **10**, 51, 65 (1887).

⁴ *Ibid.*, **31**, 98, 105 (1891).

mended as an optional official method for fertilizers containing cottonseed meal or much organic matter.¹

Treat 2 grams with sulfuric acid and mercury or mercuric oxide, as in the Kjeldahl method, using a flask graduated to 250 cc. When the digestion is complete add 150 cc. of water, boil for a few minutes, cool and make up to volume.

In 1892 the Gunning method² was adopted³ as an alternative method for the determination of nitrogen and in 1893, as a result of collaborative work of the Association, De Roode⁴ recommended that this modification of the Kjeldahl method be included as one of the methods of solution for total phosphoric acid. The modification was adopted, and the method appeared as follows:

Digest with strong sulfuric acid and such other reagents as are used in either the plain or modified Kjeldahl or Gunning method for estimating nitrogen. Do not add any potassium permanganate, but after the solution has become colorless, add about 100 cc. of water and boil for a few minutes, cool, and make up to a convenient volume; 2.5 grams of substance and a digestion flask graduated to 250 cc. are recommended. This method will be found convenient when both the nitrogen and the total phosphoric acid are to be determined in a fertilizer. In this case, after diluting to volume and mixing, a portion, for the estimation of nitrogen, may be removed with a pipet and the remainder then filtered through a dry filter and a portion taken for the determination of the total phosphoric acid.

Lord⁵ reported that the De Roode method, both in its original form and as modified for nitrates, yielded good results. This method was dropped as an official method in 1924.⁶

Solution in Aqua Regia.—Huston,⁷ as a result of collaborative work of the Association, first recommended this method of solution. It was adopted as an official method and appeared in the official methods of that year substantially as follows:

Dissolve 2 grams in 15-30 cc. of strong hydrochloric acid and 5-10 cc. of nitric acid. Boil until all phosphates are dissolved and all organic matter is destroyed; cool and dilute to 200 or 250 cc.; mix and pass through a dry filter; take an aliquot part of the filtrate corresponding to 0.25 gram, 0.50 gram or 1 gram. This method is recommended for fertilizers containing much phosphate of iron or aluminum.

¹ U. S. Dept. Agr. Chem. Bull., **31**, 180 (1891).

² *Z. anal. Chem.*, **28**, 188 (1889).

³ U. S. Dept. Agr. Div. Chem. Bull., **35**, 68, 79, 92, 202 (1892).

⁴ *Ibid.*, **38**, 15 (1893).

⁵ *Ibid.*, **38**, 34 (1892).

⁶ *J. Assoc. Official Agr. Chem.*, **8**, 621 (1925).

⁷ U. S. Dept. Agr. Div. Chem. Bull., **31**, 107 (1891).

The same year Morse stated that aqua regia (3 parts hydrochloric acid, 1 part nitric acid) acts readily with little heat upon phosphates similar to Redonda phosphate and leaves a clear residue of silica.

Ignition and Solution in Hydrochloric Acid.—The original methods of the Association of Official Agricultural Chemists prescribed that in the determination of citrate-insoluble phosphoric acid the insoluble residues from the ammonium citrate extraction should be ignited and then dissolved in concentrated hydrochloric acid.¹ This procedure has been used for acidulated goods to the present time.

Richards² reported that in the determination of total phosphoric acid mere ignition at a low heat, rather than ignition with magnesium nitrate, was sufficient to destroy all organic matter prior to solution of total phosphoric acid by nitric acid. He stated that when the fertilizer contained iron compounds ignition rendered these insoluble in nitric acid and recommended either omission of the destruction of the organic matter or moistening the ignited substance with hydrochloric acid prior to the addition of the nitric acid. He claimed that solution in nitric acid without previous ignition of the fertilizer gave results that agreed very closely with the magnesium nitrate method, and though the solution may be highly colored, yet the organic matter is sufficiently oxidized to be harmless. The same year Jenkins stated that although simple ignition would remove organic matter in many cases, in others it would not.

In 1891³ the official methods of the Association prescribed that hydrochloric acid should be used as the solvent in all cases where the material was first subjected to ignition before solution. The method of ignition and subsequent solution in hydrochloric acid for bringing total phosphoric acid in solution first appeared in the official methods in 1895,⁴ apparently without formal official adoption by the Association. It was dropped as an official method in 1924.⁵

WATER-SOLUBLE PHOSPHORIC ACID

Soon after the favorable influence of phosphoric acid fertilization upon the growth of plants became known, it was discovered that different phosphates might have the same phosphoric acid content, and yet not have the

¹ Proceedings of the Convention of Agricultural Chemists and First Annual Meeting of the Association of Official Agricultural Chemists at Philadelphia, 1884.

² U. S. Dept. Agr. Div. Chem. Bull., **12**, 24 (1886).

³ *Ibid.*, **31**, 107 (1891).

⁴ *Ibid.*, **46**, 12 (1895).

⁵ *J. Assoc. Official Agr. Chem.*, **8**, 261 (1925).

same action; in fact that they frequently affected crops in quite a different way. It was found that the phosphoric acid in phosphates of organic origin had a much more favorable influence on crop yields than that in the same quantity of mineral phosphates of the same degree of fineness because it was in a condition that was more readily soluble. The more pronounced action of the phosphates of organic origin was explained by the assumption that in these phosphates the individual particles of calcium phosphate are separated from each other by organic substances, and that upon the decomposition of the organic matter they are exposed and become more susceptible to the action of soil agents, such as water and carbon dioxide, than do the less finely divided particles of the mineral phosphates. The dissolution of the phosphates of organic origin is also promoted by the products of the decomposition of the organic matter themselves having a solvent action upon the tribasic calcium phosphate. Thus, Wöhler¹ showed that when bone meal was mixed with water and allowed to putrefy the phosphoric acid passed into solution, and Liebig pointed out that the oxalic acid in guano would free the phosphoric acid contained therein from its combination with calcium. The solution of the phosphoric acid is also facilitated by the presence in the soil of substances having an acid reaction, since calcium phosphate is easily soluble in acids. Furthermore, the acid-reacting substances such as carbon dioxide excreted by the roots of living plants have a solvent action upon the phosphate particles in their immediate vicinity. Carbon dioxide, which is continually present in the soil where organic substances are always decomposing, has been shown by the experiments of many investigators to attack all phosphates of calcium more or less.

Soon after the application of bones to the soil to provide plants with phosphoric acid came into vogue, it was observed that the finer the material that was used the greater was the effect of such fertilization. The proposal of Liebig in 1840, therefore, that the insoluble phosphoric acid in bones be rendered soluble by means of sulfuric acid, *i. e.*, in the preparation of superphosphates, could not fail to find general recognition since the phosphoric acid that had been rendered soluble could mingle much more intimately with the soil when dissolved than when in an insoluble state. For the purpose of the estimation of the value of such preparations, a distinction was therefore made between the phosphoric acid soluble in water and that still in the original or insoluble form; much greater value was ascribed to the soluble phosphoric acid while, so far as commercial deter-

¹ *Ann.*, 88, 143 (1856).

mination of price was concerned, little or no value was attached to the insoluble phosphoric acid. The determination of water-soluble phosphoric acid, therefore, was of even greater importance than that of total phosphoric acid.

In 1864 Stohmann¹ called attention to the fact that practically every German experiment station used its own procedure for the examination of fertilizers and, indeed, that almost every analyst had his own modifications, with the result that agreement was seldom possible. This was particularly true in the analysis of superphosphates, where differences of 2 per cent in the water-soluble phosphoric acid were of frequent occurrence. Since such differences could not inspire the confidence of the farmers in whose interest the work of the experiment stations was done, the adoption of a uniform method for the determination of water-soluble phosphoric acid was desirable. The method Stohmann proposed for obtaining the water-soluble phosphoric acid was the following:

If the superphosphate was dry enough, the fine material was removed by sieving and the remainder was ground in a porcelain mortar and sieved. The whole was then carefully mixed. If sieving was not possible with some superphosphates because they agglomerated in the mortar to a sticky mass, as uniform a mixture as possible was made by long continued grinding. Of the sample thus prepared 20 grams was placed in a liter flask, 800 cc. of cold water was added, and the contents of the flask were shaken at frequent intervals during 3 hours. At the expiration of the 3 hour period the volume of the fluid in the liter flask was brought to the mark, the contents were carefully mixed, and the solution was filtered through a dry plaited filter; 50 cc. of the filtrate was then taken for the determination of the phosphoric acid.

Cold water was used because a solution of monocalcium phosphate was found to decompose upon warming and to deposit a calcium salt insoluble in water and acetic acid. In addition, it was stated that there was always the danger, upon warming, of the monocalcium phosphate reacting with the dicalcium phosphate present to form insoluble compounds. The 3 hour period of digestion was chosen because experiments had shown that about 0.5 per cent more phosphoric acid was dissolved in 3 hours than in 1 hour, but that no more phosphoric acid was dissolved after 5, 12 and 24 hour digestions than after a 3 hour digestion.

According to Fresenius,² many different views prevailed among various able chemists as to the correct manner of extracting superphosphates in order to determine their water-soluble phosphoric acid. Some claimed

¹ *Z. anal. Chem.*, **3**, 184 (1864).

² *Ibid.*, **7**, 304 (1868).

that results varying by several per cent were obtained if similar uniformly mixed samples were either—

(a) introduced into a liter flask (20 grams being taken as advised by Stohmann), about 500 cc. water added, the liquid frequently shaken during 4-5 hours, permitted to stand overnight, then brought to a liter, and, after considerable shaking and standing, filtered through a dry filter paper, and 50 cc. of the filtrate used for the phosphoric acid determination, or

(b) ground with water to a very fine paste, and this paste then treated in the manner described in (a).

The reason ascribed for the difference obtained in these two procedures was that in (b) the fine grinding permitted a more complete decomposition of the tricalcium phosphate since those granules that had escaped the action of the sulfuric acid in the process of manufacture because they were not sufficiently fine, were now subjected, in consequence of being brought to a very fine state of subdivision, to the action of a solution containing free phosphoric acid and thus brought into solution. Others claimed that the grinding had no influence on the content of water-soluble phosphoric acid as determined by analysis.

To settle this important question, Fresenius carried out the following series of experiments on a comparatively dry, relatively fine-grained guano superphosphate, which had a high water-soluble phosphoric acid content.

1.—Ten grams was placed on a filter and gradually extracted with cold water till the wash water no longer gave an acid reaction. The solution was then brought to a liter and mixed.

2.—The superphosphate was ground while in the dry state and passed through a sieve with 1 mm. openings. Ten grams of the uniformly mixed powder was extracted with water as in experiment (1), and the solution was brought to a volume of 1 liter.

3.—Ten grams of the superphosphate, finely ground and sieved as in experiment (2), was placed in a 500 cc. flask, and 250 cc. of water was gradually added with shaking. After standing overnight the volume was brought to 1 liter, and the solution was shaken for a considerable time and then filtered through a dry plaited filter. It was found that the error in the analytical results when the volume of the insoluble portion was disregarded in the calculation was 0.08 per cent.

4.—Ten grams of the unground superphosphate was extracted by rubbing with a pestle in a mortar with water so as to bring about complete disintegration of the lumps but not to grind the coarser, hard particles to a fine powder. After settling, the supernatant liquid was poured through a filter, and the extraction with cold water was repeated until the liquid no longer gave an acid reaction. The extracts were finally brought to 1 liter with water and mixed.

5.—Ten grams of the unground superphosphate was ground with a little cold water in a porcelain mortar to a very fine paste and then treated further as in (4).

Of the solutions obtained by procedures 1, 2, 4, and 5, 100 cc. was taken for analysis, while but 50 cc. of the liquid obtained by the third method was used for this purpose. The liquids were evaporated to dryness in a platinum dish with the addition of sodium carbonate in slight excess and some potassium nitrate to destroy the organic matter, and the residues were then gently ignited and afterwards dissolved in dilute nitric acid. The phosphoric acid was determined by the molybdate-magnesium method (p. 143).

Since comminution of the coarser particles had not taken place in procedures 1 and 4 (only the lumps that might have been present having been broken up in method 4), the average of the results obtained by these methods (20.08 and 20.13 per cent respectively) was considered correct. The deviations from this were $+0.12$ per cent, -0.23 per cent (corrected for the volume of the insoluble material) and $+0.46$ per cent for methods 2, 3 and 5, respectively. It was concluded that grinding the superphosphate with water to a fine paste before extraction (method 5) gave too high results. The positive difference of 0.12 per cent obtained with method 2 lay within the limits of error of the method for determining the phosphoric acid.

The low result in case of method 3 was attributed to adsorption of the dissolved phosphoric acid by the insoluble residue. If the volume of the insoluble residue is disregarded in the calculation, the error was but -0.15 per cent, so that there was a partial compensation of the two errors.

Fresenius concluded as a result of these experiments that method 4, which he had previously recommended,¹ should be retained for the determination of water-soluble phosphoric acid since it can be easily and simply carried out and is free from the possible objections that the extraction might not be complete or that the quantity of water-soluble phosphoric acid is erroneously increased by the manner in which the procedure is conducted. Method 1 was subsequently recommended by Fresenius, Neubauer and Luck² for the determination of water-soluble phosphoric acid directly instead of by difference.

At the Dresden meeting of German agricultural chemists, physiologists and experiment station directors in 1871,³ it was decided to adopt the following procedure (the Dresden method), which aimed to avoid the action

¹ *Anleitung zur quantitativen Analyse*, 5th ed., p. 893.

² *Z. anal. Chem.*, **10**, 149 (1871).

³ *Landw. Vers.-Sta.*, **14**, 401 (1871).

of any free sulfuric acid that might be present upon the undecomposed calcium phosphate :

Twenty grams of superphosphate was first freed from the greater portion of its water-soluble phosphoric acid by stirring (not rubbing) with water, decanting and repeating this operation if necessary. The residue was then ground fine, washed into a liter flask, and digested 3 hours with water with frequent shaking; the liquid first poured off was then added, the flask was filled to the mark, and its contents were mixed and then filtered through a dry filter.

The time of digestion, whether 3 hours or overnight, was claimed to make no difference in the final results. Although the method of extracting on a filter was considered accurate, it was deemed inexpedient to adopt this procedure since at certain seasons (spring and fall) the work of the agricultural chemical laboratories accumulated to an extent that any procedure requiring more time than that then used was impracticable.

After a comparative study had been made of (a) the Stohmann extraction procedure, (b) the Dresden method, and (c) the method of washing on a filter (the first Fresenius procedure above), it was decided in 1872 at the Magdeburg meeting¹ to vary the extraction procedure according to the quantities of iron and aluminum the superphosphate contained, as follows :

(a) *Superphosphates with a small iron and aluminum content.*—Twenty grams of the material was crushed by pressure (not finely ground) in a mortar with the addition of some water and washed into a liter flask, and sufficient water was added for convenient shaking. After a 2 hour digestion with frequent shaking, the flask was filled to the mark, and the liquid was mixed and filtered. As customary, the volume of the undissolved residue was not considered in subsequent calculations.

(b) *Superphosphates with a large iron and aluminum content.*—Superphosphates rich in iron oxide and alumina were extracted as in (a) with the modification that the digestion was omitted and the solution filtered immediately after careful shaking.

It had been found that the entire amount of soluble phosphoric acid was taken up almost immediately by the added water and that in the case of most superphosphates the time of digestion, whether 0.5, 2, 3 or 24 hours, was immaterial. Individual cases, in which a larger amount of phosphoric acid was dissolved by the longer digestion, were opposed by others in which a constant reversion of the phosphoric acid could be observed upon prolonged contact with water. Since a decrease of the dissolved phosphoric acid was always noted after lengthy treatment of superphosphates that

¹ *Landw. Vers.-Sta.*, **16**, 223 (1873).

were rich in iron and aluminum, the necessity of immediate filtration was apparent. Consideration of the volume of the residue was neglected because this was not constant, and comparative experiments showed that the maximum error involved amounted to a difference in the results of only 0.06 per cent.

Abesser, Jani and Märcker¹ considered even the 2 hour period as unnecessarily long and gave the following directions for obtaining water-soluble phosphoric acid.

Twenty grams of the superphosphate is placed in a mortar, water is then poured over it, the agglomerated lumps are broken up without applying strong pressure, and the mixture is washed into a liter flask which is then filled to the mark with water, closed with a stopper and vigorously shaken for several minutes. The solution is filtered at once.

It was expressly stated, however, that this extraction method was not applicable to superphosphates containing considerable iron and aluminum. The leaching method of Fresenius was considered to give the most accurate results in all cases.

Erlenmeyer² called attention to the fact that monocalcium phosphate, the composition of which he had shown to be expressed by the formula $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$,³ was only completely soluble in 700 parts of water at ordinary temperatures and that small quantities of water decomposed more or less of this salt into free phosphoric acid and dicalcium phosphate, which separated in insoluble form. Consequently the procedure of extracting water-soluble phosphoric acid on a filter, which Märcker and Fresenius had considered as giving the most accurate results should only be followed in the case of superphosphates containing sufficient free phosphoric acid to prevent the decomposition of the monocalcium phosphate. If the procedure was applied to superphosphates that had no free phosphoric acid the quantity of phosphoric acid which might appear in the form of the insoluble dicalcium phosphate might be 8 per cent of that present in the form of monocalcium phosphate. He also claimed that in the case of such superphosphates the digestion methods would give correct results only when the quantity of water used was at least 700 times the weight of the monocalcium phosphate contained by them.

In view of the various objections that were being expressed against the appropriateness of the Magdeburg method, Wein, Rosch and Lehmann⁴

¹ *Z. anal. Chem.*, **12**, 239 (1873).

² *Ber.*, **9**, 1839 (1876).

³ *Jahresber. Chem.*, für 1857, 145.

⁴ *Ann.*, **198**, 290, 307 (1879).

and Wein¹ carried out a series of experiments to determine (a) the digestion necessary for complete extraction of the water-soluble phosphoric acid, (b) the suitability of the extraction upon a filter by using a Bunsen suction pump, as was customary in this procedure, and (c) the quantity of water necessary for complete extraction.

The conclusions reached after a thorough study of the subject were—

(1) With superphosphate containing much free phosphoric acid a very short period of digestion suffices to dissolve all the water-soluble phosphoric acid. Increase of the quantity of water seems unnecessary, 1000 cc. being sufficient for 20 grams of superphosphate. The leaching (filter extraction) method gives very accurate results in this case, although it is not to be recommended on account of its tediousness.

(2) Superphosphates that contain but little free phosphoric acid should be digested 2 hours to make certain that all the water-soluble phosphoric acid has been brought into solution. The leaching method on the suction filter is not applicable to these superphosphates because it gives results that are too low.

(3) Superphosphates that contain no free phosphoric acid must likewise be digested for 2 hours with 1 liter of water. The leaching method gives too low results to an even greater extent than when used with superphosphates containing a little free phosphoric acid.

(4) An increase in the quantity of water does not appear appropriate.

(5) The customary practice of digesting 20 grams of superphosphate for 2 hours with 1 liter of water should be retained since it really gives the best results.

Wattenburg¹ likewise found that the decomposition which monocalcium phosphate underwent when treated with smaller quantities of water than Erlenmeyer claimed was necessary in the digestion method was so small that it had no influence on the results.

In 1881, at a meeting of German experiment station directors, trade chemists and fertilizer manufacturers,² it was agreed that for the determination of water-soluble phosphoric acid—

(a) 20 grams of superphosphate should be slurried with water in a mortar, slight pressure of the pestle but no fine grinding should be used for breaking up the large lumps, and the whole mixture should be washed into a liter flask, which should be immediately filled to the mark;

(b) all superphosphates, without exception, should be digested at room temperature for 2 hours with frequent shaking and then filtered; and

(c) the volume of the insoluble residue should be disregarded in subsequent calculations.

¹ *Landw. Vers.-Sta.*, **23**, 374 (1879).

² *Ibid.*, **27**, 405 (1882).

At its first annual meeting in 1884, the Association of Official Agricultural Chemists¹ adopted the following method for the extraction of water-soluble phosphoric acid in superphosphates:

Bring 2 grams on a filter; add a little water; let it run out before adding more water, and repeat this treatment cautiously until no phosphate is likely to precipitate in the filter. (The washings may show turbidity after passing the filter.) When the substance is nearly washed in this manner, it is transferred to a mortar and rubbed with a rubber-tipped pestle to a homogeneous paste (but not further pulverized), then returned to the filter and washed with water until the washings no longer react acid with delicate test paper. Mix the washings. Take an aliquot (usually corresponding to one-third or one-half gram of the substance) and determine phosphoric acid as under Total Phosphoric Acid.

The idea involved in the use of the small quantities of water is to prevent the partial solution and reprecipitation of phosphoric acid from phosphates containing iron and aluminum when treated with considerable water.² If only a small quantity of water is put on the filter at a time, the iron and aluminum are carried through, while a large quantity of water would make them insoluble again and leave them on the filter. Such a precipitate was found sometimes at the apex of the filter which enveloped or might envelop small quantities of the phosphate and prevent further washing by water. To obviate this the funnel was rinsed into the mortar after most of the phosphoric acid was washed out and the substance was rubbed sufficiently with the rubber-tipped pestle to crush the smear of precipitated phosphates on the sample, but not to break down the hard lumps, and then was washed back on the filter, where the washing was completed.

In 1886, the phrase "the washings no longer react with delicate test paper" in the method of the Association was changed to read "the filtrate measures not less than 250 cc."³

The procedure of washing at first with only small quantities of water at a time and letting each addition run off before another is added was emphasized by Stubbs⁴ the following year as absolutely necessary in all superphosphates containing iron and aluminum, in order that manufacturers might receive proper value for their product in those States that assign a different value to water-soluble and citrate-soluble phosphoric acid.

¹ Proceedings of the Convention of Agricultural Chemists and First Annual Meeting of the Association of Official Agricultural Chemists at Philadelphia, 1884.

² U. S. Dept. Agr. Div. Chem. Bull., 24, 59 (1890).

³ *Ibid.*, 12, 49 (1886).

⁴ *Ibid.*, 16, 37 (1887).

Chazal¹ called attention to the dependence of the quantity of water-soluble phosphoric acid on the size of the filters used during its extraction and proposed the use of a definite size, 9 cm. He also considered the use of pumps as advantageous where much work was to be done. The official method was modified, in consequence of these suggestions, so as to provide for the use of Schleicher and Schüll No. 589 filters, 9 cm. in diameter. The use of a pump, however, was left to the judgment of the analyst. It was also directed at the same meeting that the sample be placed in a beaker, washed by decantation four or five times with not more than 10-15 cc. of water, rubbed up in the beaker with a rubber-tipped pestle to a homogeneous paste, and then washed four or five times by decantation with 10-15 cc. of water before the transfer of the residue to the filter, and finally washed with water until the filtrate measures not less than 250 cc.

In 1890 Frear² reported the results of comparative experiments using (a) simple washing on the filter and (b) washing and rubbing in a beaker. In 20 cases the mean average was 0.06 per cent in favor of the direct filter method. The length of time required was somewhat greater by the rubbing method and there was sometimes danger of excessive rubbing, especially in the hands of inexperienced chemists. In the case of samples of dissolved bone differences of 0.5 per cent and more were found when the sample was rubbed very hard in order to get a sample approximating a homogeneous paste.

This observation was confirmed by other chemists,³ and in 1891 the official method of the Association of Official Agricultural Chemists was again changed so as to eliminate all rubbing and to require washing on the filter paper alone. The method as then adopted was as follows:

Weigh 2 grams, transfer to a 9 cc. No. 589 Schleicher and Schüll filter, and wash with water, allowing all the water to pass through each time before adding more, until the filtrate measures not less than 250 cc. Mix the washings, take an aliquot portion (corresponding to 0.5 gram) and determine phosphoric acid.

This method, with minor changes, has remained the official method in the United States to the present time. It is evident from the foregoing information that all methods for obtaining water-soluble phosphoric acid in superphosphates and other fertilizers are empirical and that they have been developed as a result of much practical work.

¹ U. S. Dept. Agr. Div. Chem. Bull., **19**, 34 (1888).

² *Ibid.*, **24**, 57 (1890).

³ *Ibid.*, **31**, 114 (1891).

In 1890 the Verband landwirtschaftlicher Versuchsstationen in Germany, which was organized in 1888, adopted in its official methods¹ the procedure of treating 20 grams of superphosphate with water in a liter flask; 800 cc. of water was used, and the mixture was shaken continuously and vigorously for 30 minutes before the flask was filled to the mark and the contents were filtered. The use of rotating shaking machines was recommended, either hand driven or operated by motor, and 150 r.p.m. was taken as the standard rate. Except for slight alterations, particularly in the rate of shaking, this procedure has remained the German official method for superphosphates, although the treatment of double superphosphates was changed in 1916 to the old method of shaking at intervals for 24 hours (see p. 193).

Prior to 1889, according to Crispo,² the German method of digestion was used in Belgium. Only 10 grams of the superphosphate was used, and the digestion with frequent shaking was for a 4 hour period. In 1889, the leaching method was adopted as official. It consisted in rubbing 5 grams of the dry superphosphate in a small mortar, adding some water, and rubbing further until all hard lumps were destroyed. More water was then added, and the material was thoroughly mixed, permitted to settle, and decanted through a filter into a 500 cc. flask. This operation was repeated at least twice more, with time allowed for the liquid to pass entirely through the filter. The residue was then brought upon the filter paper and washed until the wash waters no longer gave a reaction for phosphoric acid.

The reasons advanced for discarding the method used previously were as follows:

If a superphosphate is digested with much water, the free phosphoric acid, the monocalcium phosphate, part of the gypsum, and the iron and aluminum dissolved by the sulfuric acid pass into solution, and the particles of unattacked phosphate are exposed. The phosphoric acid and the monocalcium phosphate then act upon the raw phosphate and form basic phosphates, insoluble in slightly acid water. Iron and aluminum likewise combine with a part of the originally soluble phosphoric acid to form phosphates that are insoluble in the weakly acid liquid. Thus the total quantity of phosphoric acid that has been rendered soluble in the process of manufacture by the treatment with sulfuric acid is not obtained by the digestion procedure. Although this method gives good results in the

¹ *Landw. Vers.-Sta.*, **38**, 284 (1891)

² *Z. anal. Chem.*, **30**, 301 (1891).

case of superphosphates that are free or almost free from iron and aluminum, it is not applicable to the superphosphates produced in Belgium that contain up to 4 per cent of iron oxide and alumina.

In 1913 the Verband landwirtschaftlicher Versuchsstationen decided that in the determination of water-soluble phosphoric acid it was permissible to fill the flask immediately to the mark before placing it in the rotating machine,¹ and in 1914 adopted this procedure. The treatment of double superphosphates, however, was changed in 1916 to the old method of shaking at intervals for 24 hours (see p. 193).

CITRATE-SOLUBLE PHOSPHORIC ACID

Soon after superphosphates that had been made from mineral phosphates appeared on the market, the discovery was made that the phosphoric acid rendered soluble by sulfuric acid made a more or less rapid return to an insoluble form, so that in a few months the water-soluble phosphoric acid had at times diminished to but one-third of the original quantity. This circumstance proved quite disconcerting to analysts, manufacturers and consumers, since the commercial value of the product at that time depended primarily on the water-soluble phosphoric acid and little or no value was assigned to the insoluble phosphoric acid.

It was soon found that when applied to a soil the phosphoric acid that had been soluble and had become insoluble (variously called "retrograded," "regenerated," "reduced," or "reverted" phosphoric acid) exhibited a more beneficial effect than that which had never been soluble, because it was very finely divided throughout the whole mass and therefore offered a large surface for attack by the various agents in the soil. The question, therefore, arose in 1869 at the Halle meeting of the German agricultural chemists, physiologists and directors of experiment stations whether "reverted" phosphate should be considered in the determination of the value of fertilizers. A commission appointed to settle this question decided that "only the phosphoric acid that is soluble in pure water should be called soluble phosphoric acid, while the greater or less insolubility of the phosphoric acid that depends upon the nature of the material may be indicated by mention of its origin, for example, in the case of bone preparations by designation of the phosphoric acid as bone meal phosphoric acid."²

In 1871, however, Fresenius, Neubauer and Luck,³ recognizing the justice of the desire of the manufacturers that the reverted phosphoric acid

¹ *Landw. Vers.-Sta.*, **85**, 249 (1914); **86**, 152 (1915).

² *Ibid.*, **13**, 59 (1871).

³ *Z. anal. Chem.*, **10**, 149 (1871).

be given consideration in the valuation of superphosphates, proposed the following method for the determination of the reverted phosphoric acid.

Two 2 gram portions of the superphosphate were washed separately on filters with cold water until the wash water no longer gave an acid reaction. The residue from one portion was then dissolved in hydrochloric acid, and the phosphoric acid it contained was determined by the molybdate-magnesium method or the residue was dissolved with 5 per cent sulfuric acid and the phosphoric acid determined by titration with a uranium solution. The second residue was washed into a porcelain mortar with a portion of 100 cc. of an ammonium citrate solution of specific gravity 1.09. After settling, the supernatant liquor was poured into a flask and the residue in the mortar was rubbed into as fine a paste as possible and washed into the flask with the remainder of the ammonium citrate solution. The solution was shaken frequently during a half-hour period of digestion at 30°-40° C. and filtered; the residue was washed 2 or 3 times with a mixture of equal parts of citrate solution and water, then heated with sodium carbonate, dissolved in hydrochloric acid or sulfuric acid and its phosphoric acid content determined. The citrate-soluble or reverted phosphoric acid was determined indirectly by subtracting the citrate-insoluble phosphoric acid of the second residue from the sum of the citrate-soluble and insoluble phosphoric acid in the first residue.

The foregoing procedure, in which the citrate-soluble phosphoric acid was determined by difference and which therefore became known as the "Fresenius difference method," was recommended as being much more convenient than the method requiring direct determination of the phosphoric acid that was soluble in the ammonium citrate solution. For the direct determination the solution of the citrate-soluble phosphoric acid with the wash waters was evaporated in a platinum dish to dryness, the dry residue was gradually heated, and the organic matter was finally destroyed by strong ignition after the addition of sodium carbonate, and, if necessary, occasional small quantities of potassium nitrate. After cooling, the fused mass was warmed on a water bath with a little water and washed into an evaporating dish, the small amount of calcium phosphate that adhered to the platinum dish being dissolved in a few drops of dilute nitric or sulfuric acid depending upon whether the molybdate-magnesium method or the uranium titration was then used for the determination of the phosphoric acid.

To determine the combined water-soluble and citrate-soluble phosphoric acid directly it was found necessary first to extract the superphosphate with water and then the residue with the neutral ammonium citrate solution and combine these extracts because when the citrate solution was used on the superphosphate without the preliminary extraction with water a

certain quantity of citric acid was formed as a result of reaction with the acid calcium phosphate and the undissolved calcium phosphate was attacked. As a consequence too high results were obtained.

Destruction of the ammonium citrate was considered necessary in the direct determinations because citrates and oxalates were found by König and others¹ to hinder the precipitation of ammonium phosphomolybdate and even at times to prevent it altogether.

By this time, as a result of vegetation tests, a number of directors of agricultural experiment stations, especially those in France, began to consider the reverted or citrate-soluble phosphoric acid as of equal value with the water-soluble phosphoric acid; in fertilizer control work they based the value of the superphosphate or other fertilizer, so far as phosphoric acid was concerned, on the quantity of assimilable—water-soluble + citrate-soluble—phosphoric acid that it contained. In consequence it became desirable to obtain a method for determining the sum of the water-soluble and citrate-soluble phosphoric acid in a single extract.

Joulie² devised such a method by replacing the neutral ammonium citrate solution with an ammoniacal solution, prepared by adding 500 cc. of 21.60 per cent ammonia to 400 grams of citric acid, mixing, allowing to cool and bringing the volume to 1 liter with ammonia. To determine the assimilable phosphoric acid in a superphosphate or fertilizer, a 1 gram sample was placed in a small mortar, moistened with a small quantity of the citrate solution and triturated to form as fine a paste as possible. Additional quantities of the solution were then added and mixed until 40 cc. in all had been added. The contents of the mortar were emptied into a 100 cc. flask, the mortar was washed several times with distilled water—which was then added to the flask—and the volume was brought to the mark with water. After digesting in the cold for 1 hour with frequent shaking, the extract was filtered, and 50 cc. of the filtrate was taken for the determination of the phosphoric acid which was precipitated, without previous evaporation and ignition, by the addition of magnesium chloride, and determined by the uranium titration method.

Petermann³ used a citrate solution prepared by dissolving citric acid in ammonia to a neutral reaction, bringing the concentration of the solution to a specific gravity of 1.09, and then adding 50 cc. of 25 per cent ammonia per liter. To obtain the assimilable phosphoric acid, 2 grams of

¹ *Z. anal. Chem.*, **10**, 305 (1871).

² *Mon. sci.*, (3) **3**, 563 (1873).

³ *Landw. Vers.-Sta.*, **24**, 310 (1880).

superphosphate, 1 gram of precipitated phosphate, or 5 grams of a mixed fertilizer, was placed in a mortar, 100 cc. of the citrate solution was taken and portions thereof were added with constant stirring to the sample. The mixture was then transferred to a 500 cc. flask by means of a funnel, the mortar and funnel were washed with the remainder of the citrate solution, and the flask was placed on a water bath and kept exactly 1 hour at a temperature of 35°-38° C. with frequent shaking, removed, allowed to cool several minutes, and filled to the mark. The contents of the flask were then filtered through a double filter of close-textured filter paper to prevent the passage of gypsum into the filtrate, and 100 cc. of the filtered solution was taken for the phosphoric acid determination by direct precipitation with magnesia mixture. The phosphoric acid was finally weighed as magnesium pyrophosphate.

Petermann was the first to establish by direct fertilizer experiments the parity in fertilizing value of water-soluble and citrate-soluble phosphoric acid.

In 1882, at another meeting in Halle of German agriculturists, scientists and manufacturers¹ it was agreed that the following method should be used for determining citrate-soluble phosphoric acid.

Five grams of unwashed superphosphate are ground in a mortar and washed into a 250 cc. flask with 100 cc. of Petermann's citrate solution, digested 1 hour at 40° C., filled to the mark and filtered. The phosphoric acid is determined in the filtrate.

The method developed by Mohr² differed from that recommended by Fresenius and Petermann in that the superphosphate was first washed with hot water and the residue was then digested with the citrate solution at 60°-70° C.

In the original methods adopted by the A. O. A. C.,³ citrate-soluble phosphoric acid was determined by difference in a manner very similar to the Fresenius, Neubauer and Luck procedure. Water-soluble and citrate-insoluble phosphoric acids were determined on the same 2 gram sample. The residue from the treatment with water was washed into a 150 cc. flask with 100 cc. of strictly neutral ammonium citrate solution of 1.09 density, the filter paper was shredded and added, and the flask was securely corked to prevent loss of ammonia and placed in a water bath

¹ *Landw. Vers.-Sta.*, **27**, 410 (1882).

² *Z. anal. Chem.*, **23**, 487 (1884).

³ Proceedings of the Convention of Agricultural Chemists and First Annual Meeting of the Association of Official Agricultural Chemists at Philadelphia, 1884.

with a constant temperature of 65° C. After a 30 minute digestion with frequent shaking, the warm solution was filtered quickly (not more than 20 minutes), a porous plaited filter being used and also a filter pump if necessary, and the residue on the filter was washed with water of ordinary temperature. The filter and contents were ignited to destroy organic matter, treated with concentrated hydrochloric acid, digested over a low flame until the phosphate was dissolved, diluted to 200 cc., mixed and passed through a dry filter, and an aliquot was taken for determination of the citrate-insoluble phosphoric acid by the molybdate-magnesium method. The citrate-soluble phosphoric acid was obtained by subtracting the sum of the water-soluble and the citrate-insoluble from the total. This method, therefore, required three phosphoric acid determinations—total, water-soluble and citrate-insoluble—whereas the Fresenius difference method required but two—citrate-soluble + citrate-insoluble, and citrate-insoluble.

The directions given for the preparation of the ammonium citrate solution were as follows:

Mix 370 grams of commercial citric acid with 1500 cc. of water; nearly neutralize with 410 grams of crushed commercial carbonate of ammonia; heat to expel the carbonic acid; cool; add ammonia until exactly neutral (testing for excess both of acid and alkali by aid of delicate red and blue litmus papers); and bring to a volume of 2 liters. Dilute further until the density is 1.09 as tested by the balance or an accurate specific gravity spindle.

In 1885 the committee of the Association on phosphoric acid called attention¹ to the fact that this method for extracting "reverted" phosphoric acid was originally designed for and was only applicable to superphosphates, plain or nitrogenized, and was not intended to be applied to rock phosphates, natural guanos, or any other non-acidulated materials to test their relative solubility or availability. It was recommended that a determination of citrate-insoluble phosphoric acid in non-acidulated goods be made by treating 2 grams of the phosphatic material, without previous washing with water, precisely in the way described above, unless the substance contained much animal matter (bone, fish, etc.), when the residue, insoluble in ammonium citrate, was to be ignited with magnesium nitrate before it was dissolved in acid. This recommendation was adopted at the same meeting and included in the official methods. With subsequent changes in the official methods for obtaining total phosphoric acid solutions of fertilizers containing organic matter corresponding changes were made in the treatment of the citrate-insoluble residues of non-acidulated

¹ U. S. Dept. Agr. Div. Chem. Bull., 7, 14 (1885).

goods containing much animal matter. Thus, in 1886 it was prescribed that these residues be digested with concentrated hydrochloric acid and potassium chlorate.

Richardson¹ called attention to the failure to specify the temperature at which the specific gravity of the neutral solution of ammonium citrate was determined and also to the difficulty of determining exact neutrality by the use of ordinary litmus paper and recommended that a saturated alcoholic solution of coralline be used and that the specific gravity of the citrate be determined at 20° C. The directions were accordingly changed to include these recommendations, the use of litmus paper being no longer directed.

As a result of vegetation experiments, Wagner² proposed the use of an acid ammonium citrate solution to determine "soluble" phosphoric acid in phosphatic fertilizers. A concentrated citrate solution was prepared by dissolving 150 grams of citric acid in water in a liter flask, neutralizing with ammonia, adding 10 grams of citric acid to the neutralized solution and bringing to the mark with water. The dilute citrate solution used for obtaining the "soluble" phosphoric acid was made by mixing one volume of this concentrated solution with four volumes of water. The method was carried out in the following manner:

Five grams of the sample, without previously washing with water, were rubbed up with some of the dilute citrate solution, poured into a 500 cc. flask, made to the mark with dilute citrate solution, allowed to digest about 18 hours at the temperature of the room (13°-18° C.) with frequent shaking, and then filtered; 50 cc. of the filtrate was taken, and the phosphoric acid was determined by the molybdate-magnesium method without previous destruction of organic matter.

A comparison of the results obtained by Wagner in applying the acid citrate method to various phosphatic materials with those of his vegetation tests is shown in Table XII.

TABLE XII.—"SOLUBLE" PHOSPHORIC ACID IN PHOSPHATES AS DETERMINED BY WAGNER.

	Fertilizer tests	Acid citrate method
	Per cent	Per cent
Dicalcium phosphate	30.6	29.3
Tricalcium phosphate	18.0	19.1
Water-extracted double superphosphate	17.9	16.9
Water-extracted phosphorite superphosphate	3.0	3.3
Phosphorite meal	0.1	0.6

¹ U. S. Dept. Agr. Div. Chem. Bull. 12, 21 (1886).

² Chem. Ztg., 10, 1, 19, 37 (1886).

At a meeting in 1885 of fertilizer manufacturers of Southern Germany and directors of five German agricultural experiment stations, this method for the analysis of all superphosphates was unanimously agreed upon to be used from January 1886, and the term "soluble" was adopted to designate the phosphoric acid extracted by the process.¹

The Association of Official Agricultural Chemists made a study of the results obtained by (a) using the Wagner procedure and (b) first leaching the 5 gram sample with pure water, as in the ordinary method of determining "water-soluble," and treating the residue by Wagner's method. The chairman of the Committee on Phosphoric Acid reported in 1886 as follows:² "It is very evident that Wagner's method gives much lower percentages of what we are accustomed to call 'available' P_2O_5 than the method now in use by us. The introduction of this method into our work would clearly be attended with many embarrassments; and yet if Dr. Wagner's crop experiments and his conclusions are to be relied on, it is a question if his analytical method is not a proper one to employ in the official work of experiment stations and State offices."

At the same meeting and later, Chazal³ called attention to the disadvantage in the official method of the Association of shredding the filter paper into the citrate solution, thereby causing danger of imperfect washing with water and also retarding contact of the fertilizer with citrate solution when shaken. The next year Dabney referred to various interpretations by different analysts of the time of digestion, some considering that the 30 minutes should be counted from the time the flask was placed in the water bath while others counted from the time the solution itself reached $65^{\circ} C.$; Lord suggested that the form of the flask and its size were important and proposed an Erlenmeyer flask holding 200-240 cc., and Scovell advocated the use of nitric acid for solutions of the citrate-insoluble residue.

The official method was accordingly modified to read as follows:

Wash the residue of the treatment with water into a 200 cc. flask with 100 cc. of strictly neutral ammonium citrate solution of 1.09 density. Cork the flask securely and place it in a water bath, the water of which stands at $65^{\circ} C.$ The water bath should be of such size that the introduction of the cold flask or flasks should not cause a reduction of the temperature of the bath of more than $2^{\circ} C.$ Raising the temperature as rapidly as practicable to $65^{\circ} C.$, which is subsequently maintained, digest with frequent shaking for 30 minutes from the instant of insertion, filter the warm solution quickly (best with filter-pump) and wash with water of ordinary

¹ *Chem. Ztg.*, **10**, 38 (1886).

² U. S. Dept. Agr. Bur. Chem. Bull., **12**, 18 (1886).

³ *Ibid.*, 28; **16**, 40 (1887).

temperature. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10-15 cc. of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 cc., mix, pass through a dry filter, take an aliquot and determine phosphoric acid.

In 1889¹ the directions for shaking during the digestion were made more specific at the suggestion of Battle, by stating that the flask should be shaken every 5 minutes, and in 1890² water of ordinary temperature for washing was replaced, on the recommendation of Gascoyne, by water of about the temperature of 65° C.

The Verband landwirtschaftlicher Versuchsstationen in 1890³ decided that the determination of citrate-soluble phosphoric acid was of no importance in the case of superphosphates, and from this time on only water-soluble and total phosphoric acid in superphosphates have been determined in Germany, although the citrate-soluble phosphoric acid content is determined upon request according to the Petermann procedure.

In 1891 Payne⁴ proposed the use of ammonia, instead of ammonium carbonate, in the preparation of the A. O. A. C. ammonium citrate solution and with the adoption of this recommendation the directions for the preparation of this solution became those now in use. The method of preparation involving the use of calcium chloride for determining neutrality, proposed by Huston and adopted the same year, continued in use as an optional official method until finally dropped in 1927.⁵ The Robinson method, using phenol red as indicator and a comparator, was adopted in 1920.⁶

The procedures of (a) igniting the citrate-insoluble residue with magnesium nitrate, (b) dissolving in sulfuric acid with the addition of nitrate, and (c) dissolving by the Kjeldahl method were introduced in 1891 and that of (d), dissolving in 30-35 cc. of nitric acid and 5-10 cc. of hydrochloric acid,⁷ in 1894.⁸ The last procedure was first recommended by Gaines in 1889. Procedure (c) was dropped as an official method in 1924.⁹

¹ U. S. Dept. Agr. Div. Chem. Bull., **24**, 225 (1890).

² *Ibid.*, **28**, 228 (1890).

³ *Landw. Vers.-Sta.*, **37**, 296 (1890).

⁴ U. S. Dept. Agr. Div. Chem. Bull., **31**, 113 (1891).

⁵ *J. Assoc. Official Agr. Chem.*, **11**, 32 (1928).

⁶ *Ibid.*, **5**, 92 (1921); 443 (1922); **6**, 384 (1923).

⁷ North Carolina Expt. Sta. Tech. Bull., **7**, 4 (1893).

⁸ U. S. Dept. Agr. Div. Chem. Bull., **43**, 69 (1894).

⁹ *J. Assoc. Official Agr. Chem.*, **8**, 26 (1925).

CITRIC ACID-SOLUBLE PHOSPHORIC ACID

The analysis of Thomas slag meal has occupied the attention of agricultural chemists continuously since its introduction as a fertilizer material in the early eighties.

In 1881 Märcker¹ pointed out that the strongly alkaline slags produced in the dephosphorization of cast iron by the Thomas process can be applied directly to lime deficient soils in the vicinity of the smelter. For transportation to a distance the slag must first be enriched in phosphoric acid. But it was soon recognized that the effectiveness of the Thomas slag phosphoric acid was only slightly less than that of superphosphate phosphoric acid and also that its effectiveness became the greater the more finely it was ground. The price of Thomas slag phosphoric acid in consequence rose so high that it could be shipped considerable distances without the necessity of enrichment and it was now purchased on the basis of its total phosphoric acid content and fineness. As a result Thomas slag meal began to be adulterated by the addition of raw phosphates of less value, since tests were not made of the solubility of the phosphoric acid it contained.

It was found that adulteration with Redonda phosphate could be easily detected by treatment of the suspected meal with 5 per cent citric acid, which dissolved all the phosphoric acid in Thomas slag meal but only 8-10 per cent of that in the Redonda phosphate. This method, however, was not applicable in the case of adulteration with Belgian raw phosphate because the phosphoric acid of this phosphate dissolved just as easily in the 5 per cent citric acid as did that of the Thomas slag meal.

In 1889 Wiley² was led to believe, as a result of the superior merits of basic phosphatic slags as a fertilizer, that they might be largely soluble in neutral ammonium citrate. Examination of a sample he had received showed it to contain 20.20 per cent total phosphoric acid, 12.25 per cent of which was soluble in neutral ammonium citrate. Experience, however, has shown that the neutral ammonium citrate method, although applicable to the reverted phosphoric acid in superphosphates, is of little value when applied to phosphatic slags.

Wagner³ found that an acid ammonium citrate solution easily dissolved the phosphoric acid in the Thomas slag meal, while practically none of that in Belgian phosphate was dissolved. He had already pointed out in

¹ *Z. Rübenzuckerind.*, **7**, 93 (1881).

² *J. Anal. Chem.*, **3**, 413 (1889).

³ *Düngungsfragen*. Paul Parey. Berlin, 1894.

1889, as a consequence of vegetation tests, that Thomas slag meals of different origins were of quite different effectiveness as regards plant growth. Thus a meal from Bohemia had an effective value of only 40 when compared with the effective value of a slag meal from England, considered as 100. Further experiments by Wagner,¹ confirmed these facts, and it was also established that the differences in effectiveness of Thomas slag meals were approximately proportional to the solubility of their phosphoric acid in acid ammonium citrate solution. It thus became necessary for the farmer to have a knowledge not only of the total phosphoric acid content and the fineness of the slag meal he purchased, but also of the solubility of its phosphoric acid in acid ammonium citrate.

Wagner accordingly published a modification of his acid ammonium citrate method (see section on citrate-soluble phosphoric acid)² for the determination of citrate-soluble phosphoric acid in slagmeals. Since the bases, especially free lime, varied considerably in Thomas slag meals, they would neutralize varying quantities of the free citric acid in the acid citrate solution and therefore it was considered necessary first to determine the basicity of the slag. This was done by shaking 5 grams of the meal in a 500 cc. flask for $\frac{1}{2}$ hour with 1 per cent citric acid, filtering and titrating 50 cc. of the filtrate with 0.25 *N* sodium hydroxide, phenolphthalein being used as indicator. The citrate-soluble phosphoric acid was then obtained by shaking 5 grams of the meal for 30 minutes in a half-liter flask with a quantity of 5 per cent citric acid, calculated to neutralize the basicity, 200 cc. of an acid ammonium citrate solution containing 160 grams citric acid, 28 grams of ammoniacal nitrogen per liter, and water to the mark.

This method, being too involved for fertilizer control work, Wagner recommended a second method³ for the determination of citrate-soluble phosphoric acid in Thomas slag meals and mineral phosphates, which did not consider the basicity of the phosphate and in which the citrate solution contained more free citric acid.

Five grams of the material, unground and unsieved, were placed in a half-liter flask, and the flask was filled to the mark with dilute ammonium citrate solution having a temperature of 17.5° C. The flask was closed with a rubber stopper and immediately put in a rotating machine making 30-40 r.p.m., for 30 minutes, after which the solution was at once filtered.

The stock concentrated ammonium citrate solution contained exactly 150 grams of pure crystallized citric acid and 23 grams of ammoniacal

¹ *Düngungsfragen*. Paul Parey. Berlin, 1894.

² *Chem. Ztg.*, **18**, 1153 (1894).

³ *Ibid.*, **18**, 1153 (1894); **19**, 1419 (1895).

nitrogen (27.93 grams NH_3) per liter, the latter being determined by exact analysis. The dilute ammonium citrate solution used in the analysis was made by diluting two volumes of the stock solution with three volumes of distilled water. It therefore contained 1.4 per cent free citric acid, whereas the solution used in the method first proposed after dilution contained only 0.8 per cent free citric acid.

In 1897 the A. O. A. C. published the latter method,¹ and a note to this reference was inserted in the methods of the Association.

In the meantime questions arose as to the cause of the differences in solubility and effectiveness of the Thomas slag meals from different sources and the possibility of changing the difficultly soluble Thomas meals into easily soluble ones. It was natural to consider the cause to be the difference in lime content and to assume that slags containing considerable free lime would be more easily soluble and active than those poor in lime, but this theory proved to be incorrect. Wagner² found that the silicic acid content of the slag meal determined its solubility. Thus a comparison of the citrate solubility of various Thomas slag meals with their "relative silicic acid content" (the ratio of total phosphoric acid to total silicic acid) gave the following results:

Thomas slag meal	Relative citrate solubility	Relative silicic acid content
1	100	100
2	89	100
3	90	96
4	94	96
5	48	48
6	59	55
7	52	45
8	55	52
9	47	44

It may be seen from these results that, in general, citrate solubility increases with the relative content of silicic acid. Hoyermann³ discovered independently the same relationship and found in a direct test that the citrate solubility of a Thomas slag was increased from 58 per cent to 84 per cent by the addition of sand to the molten slag.

In 1894 the Verband der landwirtschaftlichen Versuchsstationen⁴ adopted the second Wagner method for the analysis of Thomas slags as a

¹ U. S. Dept. Agr. Div. Chem. Bull., **51**, 72 (1898).

² *Chem. Ztg.*, **18**, 1511 (1894).

³ Beiträge zur Frage der Citratlöslichkeit der Phosphorsäure im Thomasschlackenmehl. Hannover, 1894.

⁴ *Chem. Ztg.*, **18**, 1588, 1933 (1894).

result of a comparison of the results of vegetation tests and of analyses by this method.

As a consequence also of Wagner's work showing the relationship between the silica content of Thomas slag meals and their solubility, the manufacturers began to produce slags having the highest silica content possible and of a composition so different that the method of determining citrate solubility no longer gave satisfactory results because the solubility of the slags no longer agreed well with their effectiveness. This condition necessitated finding a new method of analysis that would give results more in agreement with agricultural results.

Gerlach and Passon¹ showed that the active agent in the citrate solution was the free citric acid it contained, the ammonium citrate playing only a minor role, and suggested that the ammonia could be omitted. Wagner² adopted this suggestion as a result of numerous vegetation tests, and devised a new method for the determination of the effective phosphoric acid in basic slags. This method has been generally adopted and is still in use. In place of the acid ammonium citrate solution, which contained 1.4 per cent free citric acid, he now used a 2 per cent solution without any ammonium salt. This not only had the advantage of being more easily and accurately prepared, but it yielded better analytical results. Thus 28 Thomas slag meals showed in pot tests a relative effective value of 88 per cent; on treatment with 2 per cent citric acid they showed an average solubility of 89 per cent, while on treatment with the old solution the average solubility was only 83 per cent.

The Wagner citric acid method is as follows:

Five grams of the slag meal is placed in a 500 cc. flask into which 5 cc. of alcohol has been poured previously. The flask is now filled to the mark with dilute (2 per cent) citric acid solution, at 17.5° C. The flask is closed with a rubber stopper and immediately placed for 30 minutes in a rotating machine turning 30-40 times per minute. The mixture is then immediately filtered. The molybdate-magnesium method of precipitation is then used as in the former methods.

In 1911 a special committee was appointed by the Association of Official Agricultural Chemists to carry out vegetation experiments to determine the availability of the phosphoric acid contained in Thomas Bessemer basic slag phosphate and to determine whether the Wagner method (2 per cent citric acid) of analysis was a reliable procedure for measuring the avail-

¹ *Chem. Ztg.*, **20**, 87 (1896).

² *Die Bewertung der Thomaasmehl nach ihrem Gehalt an löslicher Phosphorsäure*. Berlin, 1899.

ability of the phosphoric acid in this class of products. In the final report of this committee¹ it was concluded that the availability figures established by the vegetation pot work compared favorably with the available phosphoric acid, as measured by the Wagner method for Thomas basic slag phosphate, and with the official neutral citrate of ammonia method for superphosphates.

The Wagner method was adopted as an official method by the Association in 1923.²

From the foregoing discussion it is evident that, just as in the case of water-soluble and citrate-soluble phosphoric acids, the methods for the determination of citric acid-soluble phosphoric acid have been developed in a purely empirical way. Whereas total phosphoric acid is a definite fixed quantity and different methods for its determination should give no appreciable variation in results, water-soluble, citrate-soluble and citric acid-soluble phosphoric acids are rather arbitrary quantities, and are dependent on a number of factors such as time of digestion, degree of fineness of the sample, kind and quantity of solvent, agitation, etc., which have been so chosen as to give results that harmonize with vegetation tests.

GENERAL METHODS FOR THE DETERMINATION OF PHOSPHORIC ACID

GRAVIMETRIC METHODS—(a) *Not Involving Molybdate Precipitation.*

Uranium Methods.—LeConte³ was the first to employ a uranium salt for the estimation of phosphoric acid. He used both gravimetric and volumetric procedures. The gravimetric method will be described here and the volumetric process later on under volumetric methods. The solution containing the phosphate, as nearly neutral as possible, was acidulated with acetic acid, an excess of uranium nitrate was then added, and the mixture was boiled for some minutes. Precipitation was complete in less than 5 minutes after the mixture was removed from the flame. The dense precipitate was washed by decantation with hot water, if lime was not present, or with water acidulated with acetic acid in the presence of lime. Washing was stopped when the wash water no longer gave a precipitate or color with potassium ferrocyanide. The precipitate was then dried and weighed as uranyl orthophosphate.

¹ *J. Assoc. Official Agr. Chem.*, **7**, 218 (1924).

² *Ibid.*, **6**, 254 (1923).

³ *Pharm. J. Trans.*, **13**, 180 (1853-4).

A similar procedure was used by Knop,¹ who employed uranium acetate for the precipitation. The phosphate was dissolved in hydrochloric or nitric acid and concentrated, then saturated with ammonia, and ammonium acetate was added, followed by acetic acid in large excess. The solution was treated with uranium acetate, boiled, evaporated to dryness, diluted with water and acetic acid, again boiled and filtered. The precipitate was washed, dried, ignited, and weighed as uranyl pyrophosphate.

This method is inapplicable when large quantities of iron and aluminum are present. Sutton,² using Knop's procedure but washing the precipitate by decantation, found that it gave excellent results for the determination of phosphoric acid in guanos, superphosphates, bone-ash and coprolites. Fresenius, Neubauer and Luck³ also found that the method gave good results when ferric and aluminum salts were not present. Jean⁴ prevented the simultaneous precipitation of these metals by the addition of citric acid. To facilitate the washing of the uranium precipitate, Fresenius⁵ recommended the use of a solution of ammonium nitrate as wash liquor.

Silver Methods.—In Schlösing's method⁶ the phosphates, which must not contain iron or aluminum, were mixed with silica and ignited in an atmosphere of carbon monoxide. The phosphoric acid was determined either by the loss of weight or by distillation of the phosphorus into a solution of silver nitrate heated to 80°-90° C. The solution, containing phosphoric acid, was poured into a platinum dish, and the precipitate of silver phosphide was dissolved in nitric acid; this solution was also added to that in the dish. After evaporation to dryness the residue was heated until the excess acid had been volatilized, and it was then extracted with water. The silver phosphate then remaining was dried, heated, and weighed. To make the method applicable to the determination of phosphorus in iron it was modified⁷ by igniting the iron in chlorine, condensing the volatilized phosphorus chloride, evaporating with nitric acid to convert into phosphoric acid, and then treating with silver nitrate to form silver phosphate. Volatilization of the iron was prevented by the addition of potassium chloride. This method⁸ was extended to phosphates by igniting them with ferrous

¹ *Chem. Centr.*, **1856**, 737, 769, 803.

² *Chem. News*, **1**, 97, 122 (1860).

³ *Z. anal. Chem.*, **10**, 136 (1871).

⁴ *Compt. rend.*, **78**, 1305 (1874).

⁵ *Anleitung zur quantitativen chemischen Analyse*, 6th ed., p. 820.

⁶ *Compt. rend.*, **59**, 384 (1864).

⁷ *Ibid.*, **66**, 1043 (1868).

⁸ *Ibid.*, **67**, 1247 (1868).

silicate and carbon in a carbon-lined crucible and then treating the iron phosphide in the manner just described.

Bismuth Methods.—Chancel¹ dissolved the phosphate in concentrated nitric acid, precipitated the sulfates with barium nitrate and the chlorides with silver nitrate, precipitated the excess silver, reduced the iron with hydrogen sulfide, and then added bismuth nitrate and collected, ignited, and weighed the precipitate. A number of analysts have shown that this procedure is inaccurate owing to the contamination of the precipitate by small quantities of basic salts. Birnbaum and Chojnacki² modified the method by digesting the precipitate with ammonia and ammonium sulfide, acidifying with acetic acid, boiling, filtering and, after removal of last traces of hydrogen sulfide by a few drops of chlorine water, titrating the filtrate with uranium solution.

Lead Methods.—Fischer³ precipitated the phosphoric acid from its solution, made strongly acid with acetic acid, by means of lead acetate and weighed the lead phosphate. Fresenius, Neubauer and Luck⁴ found that this procedure was inaccurate when iron and aluminum were present in the phosphoric acid solution owing to contamination of the precipitate by the phosphates of these metals. Rose⁵ states also that the composition of the lead phosphate precipitate is not constant and recommended the determination of free phosphoric acid by difference in those rare cases where the phosphoric acid solution contains only nitric acid in addition. The solution was evaporated to dryness with a weighed amount of lead oxide and ignited to decompose the lead nitrate. The difference between the final weight and the weight of the lead oxide used gave the weight of the phosphoric acid (P_2O_5) in the solution.

In the case of aqueous or acetic acid solutions of phosphates, free from sulfates and chlorides, Rose precipitated the phosphoric acid with lead nitrate or lead acetate and then determined the lead in the precipitate, obtaining the phosphoric acid by difference. Bäber⁶ stated that ferric and calcium compounds were also precipitated by this procedure.

Calcium Methods.—Rammelsburg⁷ added sulfuric acid to the sample, heated, cooled, added water and sodium carbonate, evaporated, and ignited.

¹ *Compt. rend.*, **50**, 416 (1860); **51**, 882 (1861).

² *Z. anal. Chem.*, **9**, 203 (1870).

³ *Ibid.*, **5**, 207 (1866).

⁴ *Ibid.*, **10**, 133 (1871).

⁵ *Ausführliches Handbuch der Analytischen Chemie*, 505 (1851).

⁶ *Z. anal. Chem.*, **4**, 121 (1865).

⁷ *Pogg. Ann. Phys. Chem.*, **64**, 251 (1845).

After extracting with water, ammonium carbonate was added to the solution, which was then evaporated to dryness. After extracting again with water, the phosphoric acid was precipitated with calcium chloride, and the calcium phosphate was weighed. He later modified the method by adding potassium sulfate to the solution of the sample in sulfuric acid and precipitating with 80 per cent alcohol. The precipitate was filtered off, and water was added to the filtrate, which was evaporated to remove the alcohol. The solution was then saturated with ammonia, and the phosphoric acid was precipitated with calcium chloride.

Bone black was originally used extensively in France as a fertilizer material. As its value for this purpose became better known and appreciated, its price rose and various more or less dark materials were added as adulterants until finally there were even sold so-called bone blacks that did not contain anything but carbonized peaty clay. These frauds awakened the authorities to such an extent that finally the prefecture of Nantes, principal center of the bone black industry, created a laboratory for analyzing fertilizers. Bobierre was charged with the direction of this institution. When the number of analyses increased and a rapid method of analysis became necessary, Bobierre adopted the procedure of drying the sample, igniting it, weighing out 1 gram of the ignited material, dissolving in dilute nitric acid, separating the insoluble matter by filtration, precipitating the filtrate by the addition of ammonia in excess and collecting, washing, drying, igniting and weighing the precipitate, which was considered pure tricalcium phosphate. This method was generally adopted in France under the name of the "commercial method," and when superphosphates came into general use the determination of both soluble and insoluble phosphoric acid was carried out by the same method of precipitation with ammonia with the single modification that a solution of calcium chloride was added to furnish an excess of lime to obtain complete precipitation of the phosphoric acid in the case of the soluble portion.

Although this method was used in French commercial laboratories until a comparatively late period, it finally fell into disrepute¹ because phosphatic fertilizers began to be adulterated with valueless materials containing iron and aluminum, which were also precipitated and consequently weighed as calcium phosphate.

Tzschucke² dissolved the sample in either hydrochloric or nitric acid before making the precipitation with ammonia but advised that when the

¹ Joulie, *Mon. sci.*, (3) 2, 212 (1872).

² *Z. anorg. Chem.*, 166B, 383.

phosphate contained iron and aluminum, a separate determination be made of the ferric phosphate and that the weight of this multiplied by the factor 0.53 be subtracted from the weight of the impure calcium phosphate. He likewise recommended the addition of a solution of calcium chloride to the solution of the phosphate when insufficient lime was present, as happens in the case of commercial precipitated phosphate, before the precipitation with ammonia. Silica would also cause too high results and Tzschucke recommended the method merely as a way to make a rapid preliminary determination.

In 1829 Rose¹ stated that the composition of the precipitate thrown down from solutions of phosphates by salts of calcium or lead is always uncertain and that it is therefore impossible to calculate the quantity of phosphoric acid present from the weight of the phosphates of these metals.

Aluminum Method.—In the method of Munroe² an aluminum sulfate solution of known aluminum content was added to the solution of an alkali phosphate, followed by mercuric chloride and sodium or potassium hydroxide until some mercuric oxide was precipitated. After filtering, washing and igniting, the precipitate contained only phosphoric acid and a known quantity of aluminum oxide. This method is applicable only to alkali phosphates and free phosphoric acid.

Copper Method.—Munroe also added mercurous nitrate and then mercuric nitrate to the hot nitric acid solution of the phosphate, and then added sodium hydroxide until mercuric oxide was precipitated. The precipitate was washed, dried, mixed with a weighed amount of cupric oxide and heated. The phosphoric acid was obtained by difference, the ignited precipitate containing cupric oxide and phosphoric acid only. Although aluminum salts do not interfere with this method, the presence of ferric salts renders it worthless.

Tin Method.—The determination of phosphoric acid by means of stannic phosphate was proposed by Reynoso.³ The phosphate and a weighed quantity of pure tin were boiled with nitric acid. After complete oxidation of the tin the precipitate was filtered, washed, ignited and weighed. From this weight there was subtracted the weight of stannic oxide corresponding to the tin originally used. The difference was the phosphoric acid.

¹ *Handbuch der analytischen Chemie*, 1829.

² *Am. J. Sci. Arts*, (3) 1, 329 (1871).

³ *Compt. rend.*, 33, 385 (1851).

Magnesium Methods.—The determination of phosphoric acid by precipitation as magnesium ammonium phosphate and weighing as magnesium pyrophosphate has been the most generally used gravimetric procedure from the time of the earliest analysts. The problems involved in the separation of the phosphoric acid from iron, aluminum and calcium, however, have given rise to numerous methods. These may be divided into two classes: (1) methods in which the phosphoric acid is precipitated directly as magnesium ammonium phosphate; and (2) methods in which the phosphoric acid is first precipitated as phosphates of other metals, which are then again brought into solution for final precipitation as the magnesium salt.

(1) *Magnesium Methods Involving Direct Precipitation.*—Otto¹ acidified the solution of the phosphate by the addition of oxalic or acetic acid in slight excess, removed the calcium by precipitation with ammonium oxalate, filtered, added tartaric acid to prevent the precipitation of iron and aluminum upon the addition of ammonia, and precipitated the phosphoric acid from the ammoniacal solution by the addition of a solution of magnesium ammonium chloride.

In the method of Boussingault the lime was separated by the addition of sulfuric acid and alcohol. The alcohol was then removed by long boiling, and the phosphoric acid was precipitated as magnesium ammonium phosphate, a little tartaric acid being used to prevent the precipitation of the iron and aluminum as in Otto's method. This method was stated by Joulie² to give accurate results but to require considerable time.

Fresenius³ reported that a mixture of tartaric acid, magnesium chloride, ammonium chloride and ammonia may, at certain concentrations, give a crystalline precipitate resembling that of magnesium ammonium phosphate and that, therefore, Otto's method might give erroneous results. Fresenius later recommended⁴ dissolving the precipitate in hydrochloric acid after it had been washed, adding a very little tartaric acid and again precipitating with ammonia. Will⁵ called attention to the same source of error as did also Mayer,⁶ who showed that the precipitate contained basic magnesium tartrate but that no precipitation of tartrate took place under certain definite conditions of concentration and content of ammonium salts. Accord-

¹ *Schweigg. J.*, **67**, 148 (1833).

² *Mon. sci.*, (3) **2**, 212 (1872).

³ *J. prakt. Chem.*, **45**, 258 (1848).

⁴ *Z. anal. Chem.*, **3**, 148 (1864).

⁵ *Anleitung zur Chemischen Analyse*, 2nd ed., 137.

⁶ *Ann. Chem. Pharm.*, **101**, 164 (1857).

ing to Knapp,¹ the tartrate method can not be used when more aluminum is present than corresponds to the phosphoric acid because then the precipitate of magnesium ammonium phosphate does not form at all.

Warington,² first recommended the substitution of citric acid for tartaric acid, although Fresenius³ had stated that the use of citric acid gave unsatisfactory results. In 1864⁴ Fresenius again advised against the use of citric acid when other substances were to be determined in the filtrate, as in soil analysis for which Warington had especially recommended the method. It was first shown by Brassier⁵ that the preliminary removal of calcium was not necessary in the citrate method. He proceeded as follows: The hydrochloric acid solution of the phosphate was precipitated by an excess of ammonia; the precipitate of iron, aluminum and calcium phosphates was redissolved by the addition of citric acid drop by drop while the liquid was kept ammoniacal. Magnesium chloride was then added in sufficient quantity to obtain all the phosphoric acid as magnesium ammonium phosphate. The precipitate was washed with an ammoniacal solution, dried, calcined and weighed. He states that sulfates must not be present in the solution except in traces, otherwise calcium sulfate is precipitated upon the addition of the ammonia, and also that a large excess of ammonium citrate should not be present since the magnesium ammonium phosphate is appreciably soluble in both ammonium tartrate and ammonium citrate. The results obtained were very satisfactory though slightly low when the calcium was not previously separated.

Fresenius, Neubauer and Luck,⁶ however, stated that the direct precipitation of phosphoric acid in the presence of tartaric or citric acids did not give satisfactory results because of the simultaneous precipitation of basic magnesium salts and because of the solubility of the magnesium ammonium phosphate in ammonium tartrate and ammonium citrate. In the determination of citrate-soluble phosphoric acid, therefore, they first destroyed the organic matter in the ammonium citrate solutions they obtained and used either the molybdate-magnesium, or uranium method.

With the introduction of the concepts "reverted phosphoric acid" and "soil soluble," "assimilable" or "available" phosphoric acid the question of the direct precipitation of phosphoric acid as magnesium ammonium phos-

¹ *Z. anal. Chem.*, **4**, 152 (1865).

² *J. Chem. Soc.*, **18**, 304 (1863).

³ *J. prakt. Chem.*, **45**, 258 (1848).

⁴ *Z. anal. Chem.*, **3**, 148 (1864).

⁵ *Ann. Chim. Phys.*, (4) **7**, 355 (1866).

⁶ *Z. anal. Chem.*, **10**, 137 (1871).

phate acquired additional interest since the solvent action of ammonium citrate solutions upon certain water-insoluble phosphates was employed as a means of separating such phosphoric acid from that considered of no immediate value to plants.

Joulie¹ now showed that the interference of calcium sulfate, as well as of calcium chloride, with the accuracy of the results obtained by the Brasier method could be obviated by using certain precautions with reference to the relative proportions of the reagents employed. He prepared a citro-magnesia solution from 400 grams of crystallized citric acid, 20 grams of magnesium carbonate and 200 grams of distilled water; added 500 cc. of ammonia (22° Bé.) after the magnesium carbonate had been completely dissolved, cooled and brought to a liter with water. The phosphoric acid was precipitated by the addition of this solution and ammonia. The precipitate was dissolved and titrated with a uranium solution or reprecipitated and weighed.

Classen² evaporated the hydrochloric acid solution of the phosphate to dryness to remove free acid, added a potassium oxalate solution, digested on a water bath, added acetic acid to dissolve iron oxide, heated, and added 95 per cent alcohol as long as a precipitate formed. After standing six hours the liquid was filtered, and the precipitate was washed by decantation with alcohol. The filtrate containing the phosphoric acid was evaporated to remove acetic acid and alcohol, water was added and any silica present was filtered off. The phosphoric acid in the filtrate was then precipitated by the addition of ammonia and magnesium chloride.

In the method of Teschemacher and Smith³ the phosphate was dissolved in hydrochloric acid. Ammonium sulfite was added to the solution, which was then boiled to reduce the iron. The boiling solution was poured into an acetic acid solution of oxalic and citric acids and then ammonia was added to complete the precipitation of the calcium oxalate. After reacidification with acetic acid, the precipitate was filtered off, and ammonia and magnesia mixture (200 grams of magnesium chloride and 100 grams of ammonium chloride in 1000 grams of water) were added to the filtrate. The precipitate was washed with ammonia, dissolved in hydrochloric acid with the addition of citric acid, and reprecipitated with the addition of some magnesia mixture and ammonia.

¹ *Mon. sci.*, (3) **2**, 212 (1872).

² *Z. anal. Chem.*, **18**, 373 (1879).

³ *Ibid.*, **19**, 499 (1880).

Petermann¹ who made a study of the Joulie method for the determination of citrate-soluble phosphoric acid by direct precipitation of the phosphoric acid from the ammoniacal ammonium citrate solution and its subsequent determination by titration with a uranium solution, found that the ammonium acetate formed by the solution of the precipitate in acetic acid interfered with the determination of the end point of the uranium titration by the potassium ferrocyanide and consequently the results might easily be too high. He therefore adopted the following method which retained the direct precipitation of magnesium ammonium phosphate:

To 100 cc. of the filtrate from the ammonium citrate extraction (see citrate-soluble phosphoric acid, p. 109) add 60 cc. of the usual magnesia mixture (110 grams of magnesium chloride, 140 grams of ammonium chloride, 700 grams of 10 per cent ammonia, and 1300 grams of water) while stirring constantly. Allow to stand for 12-14 hours, filter, wash, ignite, and weigh.

Since analysts engaged in fertilizer control work at this time desired to obtain a shorter way for determining the phosphoric acid in "citrate-soluble" extracts than the molybdate-magnesia method with its preliminary destruction of organic matter, Petermann's method was welcomed. That the method of direct precipitation was prone to errors, however, was clearly shown by Brunner,² who found more "citrate-soluble" phosphoric acid, as determined by the direct precipitation method, than total phosphoric in the examination of a number of coprolites. The high results, apparently due to the use of an excessive quantity of magnesia mixture, were avoided by Petermann, as stated previously, by limiting the volume of magnesia mixture to 60 cc. for 100 cc. of the "citrate-soluble" solution.

Grube and Tollens³ found that the Petermann direct precipitation of magnesium ammonium phosphate from an ammonium citrate solution did not precipitate all the phosphoric acid, and that the precipitate contained calcium and more magnesium than corresponded to magnesium ammonium phosphate. Correct results were obtained by a compensation of errors. The method, in consequence, has frequently been termed the compensation method.

Glaser,⁴ as well as Joulie and Petermann, found that sulfates did not interfere with the direct precipitation of magnesium ammonium phosphate under suitable conditions, and he actually used for the precipitation a mag-

¹ *Landw. Vers.-Sta.*, **24**, 328 (1880).

² *Z. anal. Chem.*, **19**, 144 (1880).

³ *J. Landw.*, **30**, 1 (1882).

⁴ *Z. anal. Chem.*, **24**, 178 (1885).

nesia mixture containing 140 grams of magnesium sulfate, 150 grams of ammonium sulfate, 30 grams of ammonium chloride, 350 cc. of 16 per cent ammonia and 1650 cc. of water. Ammonia was added to the phosphoric acid solution until just a slight precipitate was formed. A 50 per cent citric acid solution was then added (3-4 cc.) as in Brassier's method. The magnesia mixture was added dropwise to the cold solution and then a strong excess of ammonia was added. After 6-12 hours' standing, the precipitate was filtered off, washed with dilute ammonia (250 cc. of 16 per cent ammonia diluted to 1 liter), dissolved in dilute sulfuric acid (100 cc., 66° Bé. acid diluted to 1 liter), and again precipitated with ammonia and a little of the magnesia mixture. After the precipitate had settled out, it was filtered off, washed, ignited, and weighed. Glaser claimed that a preliminary separation of silica was unnecessary with this method, and that the results were absolutely accurate.

The following procedure was used by Aubin:¹

One gram of the pulverized sample was placed in a 200 cc. flask, along with 10 cc. of hydrochloric acid, and kept at a boil about 10 minutes. Ten cc. of a saturated solution of sodium acetate in 46 per cent acetic acid was then added, the volume was made up to 40 or 50 cc., and 2-3 grams of ammonium oxalate was added to the boiling solution. The filtrate from the calcium oxalate precipitate was cooled, made ammoniacal, 20 cc. of ammonium citrate was added to keep the iron and aluminum in solution, and the phosphoric acid was precipitated by the addition of magnesia mixture (200 grams of crystalline magnesium chloride and 150 grams of ammonium chloride in water to make 1 liter). The magnesium ammonium phosphate precipitate was filtered off, washed with ammoniacal water, dried, incinerated, and weighed. (The presence of calcium fluoride does not interfere with the determination.)

In 1890 the Verband landwirtschaftlicher Versuchsstationen² decided that the citrate, or direct method, was permissible for use in the determination of phosphoric acid in fertilizers but prescribed that the molybdate-magnesium method must be used in referee or umpire analyses. The exact directions of the citrate method, as used at the Halle Experiment Station (the Bühring method),³ were prescribed. The method is as follows:

REAGENTS

Ammonium citrate solution.—Dissolve 1500 grams of citric acid in 5000 cc. of 24 per cent ammonia and bring to a volume of 15,000 cc. with water.

Magnesia mixture.—Dissolve 500 grams of ammonium chloride and 1050 grams of magnesium chloride in 3500 cc. of 24 per cent ammonia and 6500 cc. of water.

¹ *Compt. rend.*, **100**, 1595 (1885).

² *Landw. Vers.-Sta.*, **37**, 291 (1890).

³ *Chem. Ind.*, **13**, 139 (1890).

PREPARATION OF SOLUTION

Prepare the water-soluble, citrate-soluble and total phosphoric acid solutions of the superphosphates and double superphosphates in the usual way.

In the case of insoluble phosphates, boil 5 grams of the very finely ground material with 20 cc. of concentrated nitric acid and 50 cc. of concentrated sulfuric acid for 30 minutes; after cooling, dilute to 500 cc. with water and filter. Take 50 cc. for the determination.

Prepare a total phosphoric acid solution of Thomas slag by moistening 10 grams in a porcelain dish with a little water; add 5 cc. of sulfuric acid (1 + 1) and, after caking of the mass, add 50 cc. of concentrated sulfuric acid and heat for 30 minutes, stirring at intervals. Before the mixture is completely cooled, add 50-75 cc. of water, wash into a 500 cc. flask, cool, fill to the mark, and filter. Take 50 cc. for the determination.

DETERMINATION

Superphosphates.—Add 50 cc. of the citrate solution to 50 cc. of the superphosphate solution corresponding to 1 gram of superphosphate, then add as quickly as possible 25 cc. of the magnesia mixture and shake for 30 minutes. (The filtration may be made immediately or after 2 or 3 days.)

In the case of double superphosphates, which at times contain considerable quantities of pyrophosphates, dilute 25 cc. of the phosphate solution, corresponding to 0.5 gram of the double superphosphate with 50-75 cc. of water, add 10 cc. of concentrated nitric acid and heat 1 hour; then add an excess of ammonia to the acid solution and acidify with a few drops of nitric acid; after cooling, add 50 cc. of citrate solution and 25 cc. of magnesia mixture and proceed as with superphosphates.

Insoluble Phosphates and Slags.—Add 100 cc. of the citrate solution to 50 cc. of the phosphate solution, cool, add 25 cc. of magnesia mixture, shake 30 minutes, and proceed as for superphosphates.

The use of sulfuric acid for dissolving raw phosphates instead of the generally used aqua regia has the advantage of not necessitating a separation of the silica since it is insoluble in boiling sulfuric acid. Also the aluminum is rendered practically insoluble. An additional advantage is the partial elimination of the calcium as gypsum. The use of sulfuric acid makes the citrate method applicable to raw phosphates.

After the introduction of Wagner's acid ammonium citrate extraction method for Thomas slag meals it was natural to attempt to apply the direct method of precipitation to the determination of citrate-soluble phosphoric acid in Thomas slags. Experiments by Wagner in 1894,¹ however, showed that the acid ammonium citrate extract of the Thomas slag meal could not be precipitated directly by the addition of citrate solution

¹ *Chem. Ztg.*, **18**, 1933 (1894).

and magnesia mixture since almost without exception these extracts contained silicic acid and the results were consequently too high. Böttcher¹ found, however, that the citrate method could be used with but slight modification to give accurate results. This was shown by a comparison of the results obtained by the citrate and molybdate-magnesium methods when applied to 52 Thomas slag meals. The directions given by Böttcher were essentially the same as those used for the analysis of other phosphatic fertilizers: add 50 cc. of the usual citrate solution (Märcker's) and 25 cc. of magnesia mixture (Märcker's) to 50 cc. of the citrate extract of the Thomas slag, obtained by the Wagner method, shake 30 minutes in a shaking apparatus and filter through a Gooch crucible. He emphasized, however, that after the precipitation with the citrate solution and magnesia mixture the solutions should not remain standing for hours but should be filtered as quickly as possible. He also stated that the Wagner extracts themselves should not be permitted to stand any considerable length of time but should be used the same day to give correct results by the direct precipitation method.

Märcker's citrate solution contained 110 grams of pure citric acid and 400 grams of 24 per cent ammonia per liter and was alkaline in reaction. The magnesia mixture was made by dissolving 55 grams of magnesium chloride, 105 grams of ammonium chloride, and 250 cc. of 24 per cent ammonia in sufficient water to make 1 liter, allowing to stand several days, and filtering before use.

The method developed by Böttcher was modified by Wagner² as follows and became known as the Böttcher-Wagner method.

To 50 cc. of freshly prepared citrate extract, which has not stood for more than 1 hour, add 50 cc. of citrate-containing magnesia mixture and stir 30 minutes, using the Stutzer stirring apparatus. Filter the precipitate at once, or at most after 1 hour, and treat further in the usual manner.

Prepare the citrate-containing magnesia mixture by dissolving 200 grams of citric acid in 20 per cent ammonia, diluting to 1 liter with 20 per cent ammonia, and mixing with 1 liter of magnesia mixture. Prepare the magnesia mixture by dissolving 110 grams of pure crystallized magnesium chloride and 140 grams of ammonium chloride in 700 cc. of 8 per cent ammonia and 1300 cc. of water.

The fertilizer committee of the Verband landwirtschaftlicher Versuchstationen, in 1902, recommended that the direct precipitation of the citric

¹ *Chem. Ztg.*, **21**, 168, 783, 993 (1897).

² *Ibid.*, 905.

acid extracts of Thomas slags be carried out exclusively by means of the Wagner citrate-containing magnesia mixture as given above.

Although this method of direct precipitation as a rule gave sufficiently accurate results, exceptions were found. Thus, in 1899, Wagner observed that certain Thomas slags of Bohemian origin usually contained very large quantities of silicic acid and that they could not be analyzed in this way because the precipitates frequently contained so much silica as to give results as much as 5 per cent too high. Accurate results could only be obtained by eliminating the silicic acid by evaporation of the citric acid extract with hydrochloric acid prior to the precipitation; 100 cc. of the citric acid extract was evaporated on the water bath with 7.5 cc. of hydrochloric acid (sp. gr. 1.12), or 5 cc. of concentrated hydrochloric acid, to a sirup which gave no odor of hydrochloric acid. The residue was then thoroughly stirred while still hot with 1.5-2 cc. of hydrochloric acid (sp. gr. 1.12) and dissolved in water to make 100 cc. The phosphoric acid was determined by the direct method in 50 cc. of the filtered solution. Since all Thomas slag meals did not require the preliminary elimination of silicic acid and the hydrochloric acid evaporation was troublesome, it was necessary to find a reliable procedure to distinguish the slags requiring the preliminary treatment from the others.

Kellner and Böttcher¹ found that when 50 cc. of the citric acid extracts of these high silica slags was boiled for about a minute with the addition of an equal volume of Märcker's alkaline citrate solution, containing 110 grams of citric acid and 400 grams of 24 per cent ammonia per liter,² and set aside for 5-10 minutes, a precipitate that was not entirely soluble in hydrochloric acid was obtained. Wagner³ later used the Kellner and Böttcher test to separate the silica in the course of analysis. After preliminary precipitation by boiling the citric acid extract with the citrate-containing magnesia mixture, hydrochloric acid was added. The solution was then filtered, and the phosphoric acid in the filtrate was precipitated by the addition of ammonia. This method, however, proved inaccurate because not all the silicic acid was eliminated.

At the 19th general meeting in 1903⁴ the Verband landwirtschaftlicher Versuchsstationen decided (1) that the direct, so-called Böttcher method was alone permissible, even in the case of umpire analyses, for the determination of phosphoric acid in all fertilizer materials (raw phosphate

¹ *Chem. Ztg.*, **26**, 1151 (1902).

² *Landw. Vers.-Sta.*, **42**, 105 (1893).

³ *Ibid.*, **66**, 257 (1907).

⁴ *Ibid.*, **60**, 221 (1904).

for the time being excluded); (2) that each Thomas slag meal extract should be first tested by the Kellner method; and (3) that if the test was positive the silica must be separated. The Wagner directions and the citrate-containing magnesia mixture were prescribed. It is interesting to note that the citrate solution used in the Kellner test contained 110 grams of citric acid per liter, while the citrate solution used for the direct precipitation contained 200 grams of citric acid per liter.

It was soon found that the Kellner test was not always reliable and as a consequence efforts were directed toward a simplified method for separating the silica in the case of all slags.

Naumann¹ now proposed a modification of a method of his that had been recommended by Märcker in 1896² as giving accurate results but which had not been adopted by the Verband landwirtschaftlicher Versuchsstationen because of certain minor drawbacks such as the development of nitrogen oxide fumes. This modified method, used at the Halle Control station, was as follows:

Shake 5 grams of the Thomas slag 30 minutes in a rotating apparatus with 2 per cent citric acid in a 500 cc. flask. After filtration pipet 100 cc. into a 250 cc. flask, add 8 cc. of nitric acid and boil the mixture over a small flame to about 25 cc. After cooling slightly add 25 cc. of concentrated sulfuric acid, with or without the addition of 5 cc. of concentrated nitric acid. Reheat the liquid to separate the silica and when white fumes replace the brownish-red fumes (in about 10 minutes) discontinue the boiling, and cool the solution; add water cautiously to dissolve the precipitated gypsum, and after cooling again bring the solution to the mark. After shaking and filtering, take 125 cc. of the filtrate, add a drop of rosolic acid, 50 cc. of ammonium citrate solution and 35 cc. of concentrated ammonia, cool the mixture, and add 50 cc. of 24 per cent ammonium citrate solution plus 25 cc. of magnesia mixture. Shake the mixture thirty minutes vigorously and then filter.

At the Darmstadt station the following method was devised:³

Place 100 cc. of the citric acid extract in a 200 cc. flask and add 50 cc. of citrate-magnesia mixture. Heat the flask over a small flame about 15 minutes until the silica separates, shake with a rotary motion to agglomerate the silica, heat over a larger flame to initial boiling, cool, and add 25 cc. of hydrochloric acid (sp. gr. 1.124). After allowing to stand 30 minutes with occasional shaking, bring the solution to the mark with water and shake vigorously until the floccules have disintegrated. Filter and shake 100 cc. of the filtrate 30 minutes in the Stutzer shaking machine with 50 cc. of 10 per cent ammonia. After filtering, treat the precipitate in the usual manner. The citrate-magnesia mixture was made as follows: Place

¹ *Chem. Ztg.*, **27**, 120, 155 (1903).

² *Landw. Vers.-Sta.*, **47**, 154 (1896).

³ *Ibid.*, **60**, 263 (1907).

2 kg. of citric acid and 400 grams of ammonium chloride in a 10 liter bottle and add 2 liters of water and 5 liters of 20 per cent ammonia. Stopper the bottle to prevent loss of ammonia until everything is in solution and the solution is cool. Then add 550 grams of magnesium chloride and sufficient water to make 10 liters.

Weibull¹ meanwhile found that although he got results which were in agreement when he compared the procedure of direct precipitation with magnesia mixture with the molybdate-magnesium method in the analysis of Thomas slags, too high results were obtained by the citrate method in the case of Wiborgh phosphates, because silicic acid rendered the magnesium ammonium phosphate impure. Weibull also found that a Thomas slag containing just as much silicic acid as the Wiborgh phosphate gave accurate results with the citrate method. He ascribed the difference in behavior to the large amount of iron in the solution of the Thomas slag, since that of the Wiborgh phosphate was almost free from iron, and found that correct results could be obtained for the Wiborgh phosphate by adding a solution of ferric chloride just prior to the precipitation with magnesia mixture. Subsequent work by Weibull² on a Thomas slag especially rich in silicic acid, which gave too high results by the citrate method, showed that correct results were obtainable upon the addition of ferric chloride as indicated above. Although the slag contained considerable iron, it was but slightly dissolved in the citric acid solution, since it appeared almost exclusively as manganomagnetite in an almost iron-free mass of calcium magnesium silicophosphate.

Wagner modified Weibull's directions as follows:

Fifty cubic centimeters of the citric acid extract was pipetted into a beaker, which was placed in a stirring apparatus containing cool water (12°-18° C.), and stirred at the rate of 250-300 turns per minute and 50 cc. of an iron citrate-magnesia mixture was added. The stirring was continued for 30 minutes, and the precipitate was filtered off, washed, dried, ignited, and weighed. The iron citrate-magnesia mixture was prepared by dissolving 200 grams of citric acid in 20 per cent ammonia, bringing to 1 liter with 20 per cent ammonia, and adding 1 liter of magnesia mixture and 20 cc. of a 20 per cent ferric chloride solution.

An extensive study was made by Popp, Contzen, Hofer and Mentz³ of the soluble silica in basic slags with reference to when it was "harmful," its form when "harmful," and means of rendering it harmless. They found that it was harmful only when the slag meals were poor in iron, and

¹ *Svensk. Kem. Tid.*, **14**, 135 (1902).

² *Chem. Ztg. Repertorium*, **28**, 355 (1902).

³ *Landw. Vers.-Sta.*, **79-80**, 229 (1913).

that the absolute quantity of soluble silica was of only minor importance, since even a silica content of 7 per cent could be harmful under such circumstances. They also determined that the harmful effect was due to a conversion of the silica from a crystalloid to a colloid state. The favorable action of iron in preventing the formation of colloidal silica was explained as being due to the protective colloid action of the iron citrate on the silica, the silicic acid colloiddally dissolved in the alkaline solution being kept in solution by the presence of considerable quantities of ferric ions. The frequent cause of the failure of the iron citrate method to give good results had been found at the Darmstadt station to be due to the fact that many Thomas slag meals contained such considerable quantities of decomposable sulfides that their citric acid extracts, which smelled strongly of hydrogen sulfide, gave a black precipitate of iron sulfide upon the addition of the ferric citrate solution and contaminated the phosphoric acid precipitate. Popp and his colleagues overcame this difficulty by using hydrogen peroxide. Their improved ferric citrate method was adopted by the Verband landwirtschaftlicher Versuchsstationen. It may be found on p. 196.

As stated previously, the Verband landwirtschaftlicher Versuchsstationen in 1903 adopted the citrate method for the determination of phosphoric acid in superphosphates. This method was a combination of the so-called Halle citrate procedure¹ and the Böttcher method of precipitation.² In 1913, the use of the Lorenz molybdate method was permitted for a 2 year period as an alternative procedure for the determination of water-soluble phosphoric acid in superphosphates and mixed fertilizers containing superphosphate,³ although the citrate method alone was permissible for umpire analysis. In 1916, however, the use of the citrate method only was permitted, and this is the official method in Germany at the present time for the determination of water-soluble and total phosphoric acid in superphosphates and double superphosphates. Either the citrate method or the Lorenz molybdate method may be used for the determination of citrate-soluble phosphoric acid as obtained by the Petermann method.⁴

(2) *Magnesium Methods Involving Preliminary Precipitation as Phosphates of Other Metals.*—Berzelius⁵ neutralized the hydrochloric acid solution of the phosphate with sodium carbonate and evaporated the solution

¹ *Landw. Vers.-Sta.*, **38**, 284 (1891).

² *Ibid.*, **40**, 52, 55 (1892).

³ *Ibid.*, **61**, 188 (1913); **65**, 250 (1914).

⁴ *Ibid.*, **90**, 96 (1921-1922).

⁵ *Lehrbuch der Chemie*, 4th ed., p. 95.

and the precipitate to dryness, added an equal quantity of one and a half times as much pure silica and six times as much sodium carbonate, and ignited at a red heat in a platinum crucible. Water was added to the sintered mass, and then ammonium carbonate was added; the solution, having stood for some time, was filtered. The filtrate was acidified with hydrochloric acid and ammonia was added in excess. The phosphoric acid was then precipitated with magnesia mixture. Rammelsburg¹ used a similar method.

In the method of Rose² the iron, aluminum and phosphoric acid were separated from the lime by means of barium carbonate. The precipitate was dissolved in hydrochloric acid, the barium was removed by precipitation with sulfuric acid, and the Berzelius method was followed from this point.

Fresenius³ dissolved the phosphate in hydrochloric acid, evaporated the solution to dryness, moistened with hydrochloric acid, added water, and filtered to remove silica. The solution was then boiled and, after removal from the flame, a solution of sodium sulfite was added until the color was light green. After boiling to remove sulfur dioxide and adding sodium carbonate which gave a white precipitate and an excess of sodium hydroxide, the boiling was continued until the precipitate was black and granular. The clear liquid was decanted off, and the precipitate was washed with hot water. The precipitate contained the iron, lime and a portion of the phosphoric acid, and the filtrate contained the aluminum and the remainder of the phosphoric acid.

The precipitate was dissolved in hydrochloric acid, reduced with sodium sulfite, almost neutralized with sodium carbonate and heated to boiling; a few drops of chlorine water were added, then an excess of sodium acetate and, if the fluid or precipitate was not reddish, additional chlorine water was added until it was so colored. After boiling, the precipitate was filtered hot and washed. It contained the iron and phosphoric acid and was dissolved in hydrochloric acid, reduced with sodium sulfite, boiled with excess sodium hydroxide and filtered. This filtrate contained the phosphoric acid.

The filtrate containing the aluminum and phosphoric acid was acidified, boiled after the addition of potassium chlorate, precipitated with ammonia and barium chloride was added as long as a further precipitate formed. This was filtered off, dissolved in as little hydrochloric acid as possible,

¹ *Anfangsgründe der quantitativen analytischen Chemie*, p. 119.

² *Pogg. Ann.*, **76**, 218 (1849).

³ *J. prakt. Chem.*, **45**, 257 (1848).

saturated with barium carbonate and heated; sodium hydroxide was added in excess and also sodium carbonate to precipitate any excess barium. The precipitate, which contained the phosphoric acid, free from aluminum, was filtered off and dissolved in hydrochloric acid; the barium was precipitated with dilute sulfuric acid and filtered; and the filtrate was united with the final filtrate from the treatment of the precipitate that contained the iron, lime and phosphoric acid. The combined filtrates were united and saturated with ammonia, and the phosphoric acid was precipitated with magnesium sulfate.

Schulze¹ nearly neutralized the hydrochloric acid solution which contained iron and aluminum in excess of the phosphoric acid and, after adding ammonium acetate and diluting, boiled until the iron and aluminum were precipitated as basic acetates, together with the phosphoric acid. He later² substituted ammonium formate for the ammonium acetate, thereby facilitating the washing of the precipitate. The precipitate was evaporated with a concentrated solution of potassium hydroxide and then ignited. The fused mass was treated with water when the aluminum and phosphoric acid passed into solution. The alkaline fluid was acidified with hydrochloric acid, tartaric acid was added, and the phosphoric acid was precipitated with magnesia mixture.

A method recommended by Rose,³ but which cannot be used in the presence of aluminum, is to add an excess of mercury to the nitric acid solution of the phosphate and heat until the nitric acid is completely driven off. The portion insoluble in water, consisting of mercurous phosphate, basic mercurous nitrate and mercury, is mixed with potassium or sodium carbonate and carefully heated until the mercury has been driven off and the nitrates decomposed. The mixture is then heated to fusion to decompose the mercurous phosphate, cooled, treated with water, and filtered if necessary. Magnesia mixture is added to the filtrate.

Chancel⁴ dissolved the phosphate in a slight excess of nitric acid, diluted the solution with water and added silver nitrate and silver carbonate. The silver phosphate was filtered off, washed and dissolved in nitric acid; the silver was precipitated with hydrochloric acid and the filtrate was made alkaline with ammonia. The phosphoric acid was then precipitated with magnesia mixture. Because iron and aluminum precipitate with the silver phosphate, the method can not be used when these metals are present.

¹ *Jahrb. Akademie Eldena*, **1**, 306 (1848).

² *Chem. Centr.*, **1861**, 3.

³ *Ausführliches Handbuch der analytischen Chemie*, Vol. II, p. 527. 1851.

⁴ *Compt. rend.*, **49**, 997 (1859).

The Chancel bismuth method was modified by Adriaansz¹ by adding sodium thiosulfate to the hydrochloric acid solution of the phosphoric acid, having an excess of aluminum present, and heating, after the iron was completely reduced, to precipitate the phosphoric acid. The precipitate was washed and dissolved in nitric acid, a little silver nitrate and barium nitrate being added to remove chlorides and sulfates. The solution was then filtered, strongly diluted, treated with bismuth nitrate, heated 2-3 hours on the water bath, and allowed to stand for several days. The precipitate of bismuth phosphate, containing some iron and aluminum, was filtered off and dissolved in hydrochloric acid. The solution was treated with hydrogen sulfide to remove bismuth and filtered, and the filtrate was heated to drive off the excess hydrogen sulfide. The iron was oxidized by the addition of a few drops of nitric acid, and the phosphoric acid was finally precipitated with magnesia mixture after the addition of a little citric acid.

In Warington's² procedure the phosphate was fused with silica and dissolved in nitric acid, ammonia was added to remove an unnecessary excess of acid and then an excess of lead acetate was added, or the solution was digested with successive portions of litharge, after the addition of lead nitrate, until it was slightly alkaline. In the latter case the solution was finally acidified with a few drops of acetic acid. After washing the precipitated lead phosphate by decantation with warm water containing ammonium acetate, it was either (1) dissolved in nitric acid and the lead precipitated with hydrogen sulfide, (2) dissolved in nitric acid and the lead precipitated with sulfuric acid, or (3) treated with an oxalic acid solution and a few drops of potassium oxalate (applicable only to the precipitate formed with lead acetate). After removal of the lead, citric acid and an excess of ammonia were added to the filtrate, and finally magnesia mixture was added.

Reissig³ improved Reynoso's method (see p. 122) as follows: The phosphate was dissolved in concentrated nitric acid and the solution, with tin-foil added, was warmed for 5-6 hours. The precipitate was then digested in a platinum dish with a potassium hydroxide solution, which converted it into potassium metastannate and potassium phosphate, both of which dissolved upon the addition of hot water. The solution was diluted and treated with hydrogen sulfide; after the addition of some ammonium sulfide, acetic acid was added until the tin was precipitated as sulfide and the solution was slightly acid. An aliquot portion of the filtrate from this

¹ *Z. anal. Chem.*, **10**, 473 (1871).

² *Chem. News*, **10**, 1 (1864).

³ *Ann. Chem. Pharm.*, **98**, 339 (1856).

precipitate was then evaporated to a small volume, and the phosphoric acid was precipitated as magnesium ammonium phosphate.

According to Girard¹ almost all the iron and aluminum are precipitated in Reynoso's method. To avoid errors due to this cause, he dissolved the precipitate in aqua regia and treated with an excess of ammonia and ammonium sulfide, thereby precipitating the iron and aluminum with the tin. After standing 30 minutes the precipitate was filtered off and washed with an ammonium sulfide solution. Magnesium sulfate was then added to the filtrate to precipitate the magnesium ammonium phosphate.

Schulze² dissolved the phosphate, after ignition to destroy organic matter, in hydrochloric acid; filtered; nearly neutralized with dilute ammonia; added antimony pentachloride, while stirring; and allowed to stand 12-24 hours. The precipitate was washed, boiled with a sodium hydroxide solution containing a little sodium silicate, and filtered. Hydrochloric acid and then ammonia were added to the filtrate, which was concentrated and treated with more ammonia, and the precipitate was filtered off. Since it contained a small quantity of phosphoric acid it was redissolved in a little hydrochloric acid, the solution was evaporated to dryness and the residue was warmed with a little acidulated water. After filtering, a small quantity of tartaric acid was added to the filtrate, which was then mixed with the preceding ammoniacal filtrate containing most of the phosphoric acid. The phosphoric acid was now separated from the combined solutions in the usual manner as magnesium ammonium phosphate.

GRAVIMETRIC METHODS—(b) *Involving Molybdate Precipitation*

Direct Weighing Methods.—A yellow precipitate of ammonium phosphomolybdate forms when a solution of ammonium molybdate in nitric acid is added to a solution of a phosphate. The composition of this precipitate varies with the conditions under which it is formed and the treatment to which it is subjected previous to weighing. The formula usually assigned to the precipitate is $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, which contains 3.784 per cent phosphoric acid (P_2O_5). The variability of the composition of the precipitate, as prepared by different analysts, is well illustrated by the fact that Sonnenschein³ found that it contained 3.03 per cent P_2O_5 ; Seligsohn,⁴

¹ *Compt. rend.*, **54**, 468 (1862).

² *Ann. Chem. Pharm.*, **109**, 171 (1859).

³ *J. prakt. Chem.*, **53**, 342 (1851).

⁴ *Ibid.*, **67**, 473 (1856).

3.14 per cent; Sopp,¹ 3.20 per cent, and Gladding,² 3.76 per cent. Under precisely determined conditions, however, the precipitate has, within certain limits, a constant composition, and a number of methods involving the direct weighing of the yellow precipitate have been used extensively.

In the method of Eggertz³ the phosphoric acid was precipitated at ordinary temperatures and digested in a bath at 40° C. for 2-3 hours with stirring from time to time. The yellow precipitate was collected on a tared filter paper, washed with water containing 1 per cent of nitric acid, and, after drying at 95° C., was weighed. Thus prepared, it contained 3.74 per cent P_2O_5 .

Lipowitz⁴ precipitated from a boiling solution by means of a molybdate solution containing tartaric acid and dried the precipitate at 20°-30° C., preferably over sulfuric acid. It contained 3.607 per cent P_2O_5 . Lipowitz was the first to show that the inconstancy of composition of the precipitate was due to occlusions of molybdic acid.

Finkener⁵ washed the precipitate, made at ordinary temperatures, with a 20 per cent solution of ammonium nitrate, which at first contained one-thirtieth its volume of nitric acid. The ammonium nitrate was mostly removed with water, and the precipitate was washed into a porcelain crucible, that adhering to the filter being dissolved in warm dilute ammonia. Concentrated nitric acid was then added in excess, and after evaporation the ammonium nitrate was removed by heating over a flame, the crucible being protected by a wire gauze. The hygroscopic residue was then cooled over sulfuric acid in a desiccator and quickly weighed in the covered crucible. The precipitate contained 3.794 per cent P_2O_5 .

Ammonium citrate was employed by Pellet⁶ who claimed that the presence of this salt insured the formation of ammonium phosphomolybdate precipitates of constant composition, corresponding to the formula $P_2O_5 \cdot (NH_4)_2O \cdot 24MoO_3 \cdot 3H_2O$ and containing 3.75 per cent P_2O_5 .

Hundeshagen⁷ washed the precipitate with a 5 per cent solution of ammonium nitrate, slightly acidulated with nitric acid and dissolved in warm dilute ammonia. If the precipitate was washed off the filter, as was done by Finkener, the solution had to be filtered to remove fibers of paper. The filtrate was received in a crucible and evaporated with the washings until

¹ *Landw. Mittheilung.*, **1**, 62 (1858).

² *J. Am. Chem. Soc.*, **18**, 23 (1896).

³ *J. prakt. Chem.*, **79**, 496 (1860).

⁴ *Pogg. Ann.*, **119**, 135 (1860).

⁵ *Ber.*, **11**, 1638 (1878).

⁶ *Bull. Assoc. Belge Chim.*, **3**, 51 (1888-9).

⁷ *Z. anal. Chem.*, **28**, 141 (1889).

the liquid retained only a faint odor of ammonia. Dilute nitric acid was then added to precipitate the phosphomolybdate. Evaporation was carried out as directed by Finkener. The thick residue was at first heated gently over a wire gauze and afterward, when it ceased to froth, more strongly until the ammonium nitrate was completely expelled. The temperature of the crucible was permitted to reach 160° - 180° C. The complete volatilization of the ammonium nitrate was indicated by the absence of a coating on a watch-glass when placed for 30 seconds on the crucible. The crucible with the precipitate was then cooled in a desiccator and weighed with the cover on. The precipitate contained 3.753 per cent P_2O_5 .

A molybdate solution prepared from 100 grams of molybdic acid, 1 liter of 10 per cent ammonia and 1.5 liters of nitric acid (sp. gr. 1.246) was used by Hanamann.¹ The molybdate solution was added without heating, and the precipitate was stirred vigorously for 30 minutes at room temperature. After washing the precipitate with an ammonium nitrate solution containing nitric acid and drying, it was gently ignited below redness in a platinum crucible over a platinum wire screen until it had a blue-black color and was of constant composition. The precipitate then contained 4.018 per cent P_2O_5 . It was sometimes necessary to moisten the ignited precipitate with ammonia, dry and reheat in order to get the correct color. Organic matter in the phosphate was previously destroyed by boiling with nitric or chromic acid.

Meinecke,² who had shown in 1885³ that the blue-black compound could be obtained on gentle heating and had given it the empirical formula, $P_2O_5 \cdot Mo_{24}O_{68}$, with a P_2O_5 content of 4.018 per cent, now found, as a result of additional work on the analysis of phosphates, that the composition of the compound was comparatively simple, namely $P_2O_5 \cdot 24MoO_3$, with a P_2O_5 content of 3.944 per cent. The original procedure of analysis was but slightly modified. The molybdate solution was prepared by dissolving 150 grams of ammonium molybdate in 150 cc. of ammonia (sp. gr. 0.91) and 850 cc. of water and pouring this mixture, with shaking, into 1 liter of nitric acid (sp. gr. 1.20). After warming for 10 minutes at 90° C., the solution was decanted and filtered. To the solution containing the phosphoric acid to be determined, ammonia (sp. gr. 0.91) and then nitric acid (sp. gr. 1.4) were added so as to obtain a solution containing approximately 5 per cent ammonium nitrate with a slight excess

¹ *Chem. Ztg.*, **19**, 553 (1895).

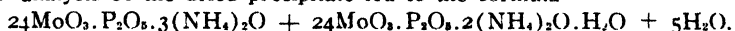
² *Ibid.*, **20**, 108 (1896).

³ *Répert. anal. Chem.*, **5**, 153 (1885).

of nitric acid. The solution was cooled to 50° C., the molybdate solution was added (100 cc. for each 0.1 gram P_2O_5), and after continued vigorous stirring the precipitate was allowed to settle. For phosphoric acid solutions containing considerable iron a higher temperature and a greater excess of free nitric acid were necessary. The solution in such cases was heated to boiling before precipitation and contained at least 10 per cent ammonium nitrate and 5-10 cc. excess nitric acid (sp. gr. 1.40) per 100 cc. The precipitate in either case was filtered and washed with an ammonium nitrate solution (equal volumes of ammonia (sp. gr. 0.91) and nitric acid (sp. gr. 1.4) diluted to 1 liter) and then with water. Finally 96 per cent alcohol or an ether-alcohol wash fluid was used. The precipitate and filter were placed in a platinum or porcelain crucible and ignited at a faint red heat, cooled in a desiccator and weighed.

The following procedure was used by Gladding.¹

To the solution of phosphoric acid add 25 cc. of strong ammonia (sp. gr. 0.900) and nitric acid (sp. gr. 1.42) to acidity. Place the beaker containing the solution in a water bath maintained at a constant temperature of 50° C. Add an excess of about 10 cc. of the ordinary 10 per cent acid molybdate solution from a buret at the rate of about 3 drops per second, with constant stirring. Allow the beaker to remain for 10 minutes in the bath and then filter its contents through a weighed filter paper. Wash the precipitate with dilute nitric acid (1 + 100) and finally with distilled water. Then drain the paper and contents for a few minutes on some waste filter or blotting paper and dry to a constant weight at a temperature of 105° C. Careful analysis of the dried precipitate led to the formula—



Gladding afterwards² recommended two final washings with alcohol to facilitate the drying, which was done in a glycerol bath at 105° C.

A study of Gladding's method of weighing the yellow precipitate directly was made by the Association of Official Agricultural Chemists in 1896 and in 1897, but the results reported by the members of this association did not show any advantages over other methods in use.³

Woy⁴ introduced the use of the Gooch crucible in the filtration of the yellow precipitate. He used as reagents (1) a 3 per cent solution of ammonium molybdate, prepared by dissolving 120 grams of ammonium molybdate in water to make 4 liters and filtering; (2) an ammonium nitrate solution made by dissolving 340 grams of ammonium nitrate in water to 1

¹ *J. Am. Chem. Soc.*, **18**, 23 (1896).

² *U. S. Dept. Agr. Div. Chem. Bull.*, **51**, 47 (1898).

³ *Ibid.*, **57**, 68 (1899).

⁴ *Chem. Ztg.*, **21**, 440, 469 (1897).

liter; (3) nitric acid (sp. gr. 1.153) containing 25 per cent nitric acid; and (4) a wash liquor containing 5 per cent ammonium nitrate and 1 per cent nitric acid (200 grams of ammonium nitrate and 160 cc. of nitric acid diluted to 4 liters). For the determination of the water-soluble phosphoric acid in superphosphates the following procedure was used:

Heat 25 cc. of the solution prepared from 20 grams of the superphosphate with 10 cc. of nitric acid and 30 cc. of ammonium nitrate to boiling and precipitate with constant stirring by adding 100 cc. of the boiling 3 per cent molybdate solution in a thin stream from a dropping funnel into the middle of the solution. Wash the precipitate once by decantation with 50 cc. of the hot wash liquor, dissolve in 10 cc. of 8 per cent ammonia and, after the addition of 20 cc. of ammonium nitrate, 30 cc. of water and 1 cc. of molybdate solution, again bring to boiling and precipitate by adding 20 cc. of nitric acid. Filter the precipitate after 15 minutes through a porcelain Gooch crucible and wash with 50 cc. of hot wash liquor, then with alcohol and finally with ether. Place the Gooch crucible in a nickel crucible on the bottom of which rests a porcelain perforated plate. Heat the nickel crucible gently to drive off alcohol and ether and gradually raise its temperature by increasing the flame until its bottom is brought to a dark red heat. Maintain this heat for 15 minutes, then cool and weigh the precipitate. The precipitate contains 3.946 per cent P_2O_5 .

In the determination of citrate-soluble phosphoric acid Woy treated 50 cc. of the solution prepared by the Wagner procedure (p. 111) with 30 cc. of nitric acid, 45 cc. of the ammonium nitrate solution and 100 cc. of a 6 per cent molybdate solution.

According to Neumann¹ the method of Woy gave too low results in the determination of Thomas slag phosphoric acid because the solution of the yellow precipitate in ammonia was not clear, and on heating to boiling it became completely cloudy as the result of the precipitation of ferric phosphate. Neumann found that Hanamann's method of precipitation in the cold with stirring gave excellent results, but he used a Gooch crucible instead of filter paper and washed with Woy's wash liquor. The Gooch crucible was placed in a larger porcelain crucible, which was heated gradually until the precipitate was blue black. A 7.5 per cent molybdate solution, as used by Meinecke, was employed instead of the 3 per cent solution of Woy; 100 cc. for each 0.1 gram of P_2O_5 was used and stirring was continued for only 15 minutes. The factor used was 0.039466.

Hanamann² subsequently used the Wagner-Stutzer molybdate solution (150 grams of ammonium molybdate and 400 grams of ammonium nitrate diluted with 2 liters of water and poured into a liter of nitric acid (sp.

¹ *Z. anal. Chem.*, **37**, 303 (1898).

² *Z. landw. Versuchsw.*, **3**, 53 (1900).

gr. 1.19)) of which he added 100 cc. for each 0.1 gram of phosphoric acid (P_2O_5), heated to $40^\circ C.$, stirred 10 minutes, filtered through a Gooch crucible, and washed with acid ammonium nitrate solution and alcohol. The factor used was 0.03946.

The Lorenz¹ method was adopted in 1908 after numerous tests² had been made to prove its reliability as an official method for the analysis of Thomas slag by the Verband der landwirtschaftlichen Versuchsstationen.³ Details of this method, as adopted by the Verein Deutscher Dünger-Fabrikanten and modified only with respect to the use of acetone in place of alcohol and ether as wash fluids for the yellow precipitate, may be found on pp. 201-4. In the original method⁴ the precipitate was washed first about 4 times with the 2 per cent ammonium nitrate solution, and the crucible was then filled full once and about half-full twice with 90-95 per cent alcohol, the filter being sucked almost dry each time. This procedure was followed by similar treatment with ether. Alcohol and ether that left no residue on evaporation and gave no alkaline reaction were prescribed. In addition, the ether was not to contain alcohol or too much water, 150 cc. dissolving 1 cc. of water completely without any turbidity.

Graftiau,⁵ like Pellet, used ammonium citrate to insure obtaining a yellow precipitate of constant composition. The acid solution of the phosphate was nearly neutralized with ammonia, the precipitate formed was redissolved with a few drops of nitric acid, and 10 cc. of Petermann's ammonium citrate solution was added. The precipitation was then made as in the determination of citrate-soluble phosphoric acid, the solution being heated to boiling. The precipitate was washed with 1 per cent nitric acid and dried 2 hours at 105° - $110^\circ C.$

Neubauer and Lückér⁶ found that when acetone was substituted for alcohol and ether in the Lorenz method for washing the yellow precipitate just as accurate results were obtained, and this modification had the advantage of being more convenient and rapid since but one wash liquor was necessary and the acetone ran through the filter rapidly. An additional advantage was the easy recovery of the acetone in contrast to the difficulty of recovering the alcohol and ether in pure states. Details of this method

¹ *Landw. Vers.-Sta.*, **55**, 183 (1901).

² *Ibid.*, **63**, 141 (1905); **66**, 203 (1907); **68**, 90 (1908).

³ *Ibid.*, **71**, 223 (1908).

⁴ *Oesterr. Chem.-Ztg.*, **14**, 1 (1911).

⁵ Atti. VI Congresso internaz. chim. applic., Rome, **1**, 64 (1906).

⁶ *Z. anal. Chem.*, **51**, 161 (1912).

are given under the methods of the Verein Deutscher Dünger-Fabrikanten. (p. 201).

Molybdate-Magnesium Methods.—The molybdate-magnesium methods for the gravimetric determination of phosphoric acid involve the successive steps of separating the phosphoric acid from the solution containing it by precipitating as ammonium phosphomolybdate, dissolving the yellow precipitate in aqueous ammonia and reprecipitating the phosphoric acid as magnesium ammonium phosphate. This procedure was first proposed by the German chemist, Sonnenschein,¹ in 1851. For convenience the method will be considered under the two sections (1) precipitation of the ammonium phosphomolybdate and (2) precipitation of the magnesium ammonium phosphate.

(1) *Precipitation of the Ammonium Phosphomolybdate.*—Sonnenschein dissolved the phosphate in nitric acid, or added nitric acid to the solution containing the phosphoric acid, and then added an ammonium molybdate solution containing nitric acid until the quantity of molybdic acid used was 30 times that of the phosphoric acid to be precipitated. The molybdate solution was made by dissolving 1 part of molybdic acid in 8 parts of aqua ammonia and then pouring this solution into 20 parts of nitric acid of specific gravity 1.2. The precipitate was digested for several hours at a gentle heat before it was filtered off. After filtration the precipitate was washed with additional molybdate solution.

The use of 60 times as much molybdic acid as phosphoric acid was recommended by Fresenius,² and Caldwell³ in addition advised that the phosphoric acid in the solution should not exceed 0.1 gram. The molybdate solution, prepared as directed by Sonnenschein, was allowed to stand for several days in a warm place, and the clear liquid was decanted off for use. It contained 5 per cent molybdic acid. The precipitate was digested for 12 hours at a temperature of about 40° C. A portion of the clear supernatant liquid was tested by adding an equal volume of molybdate solution and warming at 40° C. for 1 hour. If more precipitate formed, additional molybdate solution was added to the beaker and the digestion was continued. The filtered precipitate was washed with a mixture of 100 parts of the molybdate solution, 20 parts of nitric acid (sp. gr. 1.2) and 80 parts of water until, in case lime was present, the washings gave no turbidity in strong alcohol to which sulfuric acid had been added.

¹ *J. prakt. Chem.*, **53**, 339 (1851).

² *Z. anal. Chem.*, **6**, 403 (1867).

³ *Agricultural Qualitative and Quantitative Chemical Analysis*, p. 85. 1869.

Abesser, Jani and Märcker¹ showed that a 4-6 hour digestion was sufficient to precipitate all the phosphoric acid. From 0.1 to 0.2 gram of phosphoric acid was recommended for precipitation, and the concentration of the phosphoric acid solution was such that this quantity was contained in 50-100 cc. The molybdate solution was prepared according to the directions of Fresenius² by dissolving 150 grams of ammonium molybdate in 1 liter of water and pouring into a liter of nitric acid (sp. gr. 1.2); 50 parts of molybdic acid were used for 1 part of phosphoric acid. Since the commercial ammonium molybdate contained about 83 per cent molybdic acid about 100 cc. of the molybdic solution was necessary for each 0.1 gram of phosphoric acid. The precipitate was digested at 50° C. and then allowed to cool. After filtration the precipitate was washed with a mixture of 1 part of the molybdate solution and 3 parts of water.

In the method of Chevron³ citrate-soluble phosphoric acid was precipitated from its solution directly as ammonium phosphomolybdate by the Sonnenschein method without previous destruction of the organic matter. This procedure, however, was claimed by others to give incorrect results.

Peitzsch, Rohn and Wagner⁴ used the same procedure as Abesser, Jani and Märcker but brought the precipitate and solution to about 80° C. while stirring at frequent intervals. After cooling for an hour the precipitate was filtered off.

Stünkel, Wetzke and Wagner⁵ freed the phosphoric acid solution from silicic acid and then added an ammonium nitrate solution before the addition of the molybdate solution, of which 50 cc. instead of 100 cc. was used per 0.1 gram of phosphoric acid (P_2O_5) present. The ammonium nitrate solution contained 750 grams per liter, and it was added so that the final mixture contained 15 per cent of ammonium nitrate. The solution containing the precipitated phosphate was heated to 80°-90°C., allowed to stand for 1 hour, filtered, and the precipitate was washed with an ammonium nitrate solution containing 100 grams of ammonium nitrate per liter.

The ammonium nitrate was used in the determination because it hastened precipitation and less nitric acid and molybdate were required. Richters⁶

¹ *Z. anal. Chem.*, **12**, 239 (1873).

² *Anleitung zur quantitativen chemischen Analyse*, 6th ed.

³ *Bull. acad. roy. Belge*, **47**, 98 (1879).

⁴ *Z. anal. Chem.*, **19**, 444 (1880).

⁵ *Ibid.*, **21**, 353 (1882).

⁶ *Ibid.*, **10**, 471 (1871).

had shown the advantage of using this salt, and Gilbert¹ had advised the use of a molybdate solution containing considerable ammonium nitrate.

In the original official method of the Association of Official Agricultural Chemists the acid solution of the phosphate was neutralized with ammonia, 15 grams of dry ammonium nitrate was added, and to the hot solution 50 cc. of molybdate solution was added for each decigram of phosphoric acid (P_2O_5). After digestion for 1 hour at 65° C. the precipitate was filtered off and washed with a dilute ammonium nitrate solution as already described. This procedure is practically the same as that used by the Association at the present time.

Mohr² precipitated citrate-soluble phosphoric acid by adding an equal volume of concentrated nitric acid to the solution and then digesting for 1 hour at 85° C. with an excess of molybdate solution. After cooling, the precipitate was filtered off and the procedure continued in the usual manner. The digestion of the strong nitric acid solution destroyed the organic matter more conveniently than did the Fresenius procedure of evaporation and ignition.

Ross³ removed the citric acid from the citrate-soluble solution by diluting the filtrate and washings from the ammonium citrate digestion at 65° C. to 200 cc., diluting 50 cc. of the resultant solution to 100 cc., adding a neutral 20 per cent calcium chloride solution in excess, heating nearly to boiling with stirring, filtering off the calcium citrate, and washing it with hot water. Ammonium hydroxide in slight excess and 15 grams of ammonium nitrate were then added to the filtrate before precipitating with the molybdate solution.

(2) *Precipitation of the Magnesium Ammonium Phosphate.*—Sonnenschein⁴ dissolved the yellow precipitate from the filter with aqua ammonia and then precipitated the phosphoric acid from the ammoniacal solution with a magnesium salt. No details are given in the abstract cited, and the original thesis is not available.

Fresenius⁵ dissolved the precipitate in as little aqueous ammonia (sp. gr. 0.96) as possible, washed the filter thoroughly with a mixture of 3 parts of water and 1 part of aqueous ammonia, added hydrochloric acid cautiously and dropwise to the solution until the yellow precipitate that formed dissolved rather slowly, and then added the magnesia mixture.

¹ *Corres. Ver. anal. Chem.*, No. 1 (1878).

² *Z. anal. Chem.*, **23**, 487 (1884).

³ U. S. Dept. Agr. Div. Chem. Bull., **7**, 19 (1885).

⁴ *Loc. cit.*

⁵ *Z. anal. Chem.*, **6**, 403 (1867).

This was a solution containing 1 part of crystallized magnesium sulfate, 1 part of ammonium chloride, 8 parts of water and 4 parts of aqua ammonia, which after standing some time had been filtered if necessary. Ten cc. of this mixture was considered sufficient for a 0.5 gram sample of phosphorite containing 25-35 per cent phosphoric acid (P_2O_5). Dilute ammonia, 3 parts of water to 1 part of aqua ammonia (sp. gr. 0.96), was then added until the volume was about 110 cc., and allowed to stand for 12 hours. The precipitate was filtered off, washed with dilute ammonia until 5 drops of the wash liquor gave no opalescence with silver nitrate, dried, ignited, and weighed. A positive correction of 0.002 gram was made on the final weight of the magnesium pyrophosphate since Fresenius, as a result of previous work,¹ considered an equivalent weight of magnesium ammonium phosphate had been dissolved in the 110 cc. of filtrate.

This correction was shown to be unnecessary by Kubel² and Heintz³ who recommended solution of the magnesium ammonium phosphate in acid and reprecipitation by the addition of ammonia since a magnesia mixture made from magnesium sulfate gave precipitates that contained an excess of magnesia.

Kissel⁴ and Schumann⁵ found that correct results were obtainable in a single precipitation with a magnesia mixture containing magnesium sulfate but only as a result of the compensation of two sources of error. The precipitate contained basic magnesium sulfate as an impurity, but more of the precipitate dissolved in the presence of ammonium chloride than in a pure ammoniacal liquor and these counteracted each other. To obtain accurate results an excess of the magnesia mixture was to be avoided.

Abesser, Jani and Märcker⁶ avoided the difficulties involved in the use of the magnesium sulfate magnesia mixture by substituting magnesium chloride for the magnesium sulfate. The magnesia mixture that they prepared contained 110 grams of crystallized magnesium chloride, 140 grams of ammonium chloride, 700 grams of concentrated ammonia and 1300 grams of water. The yellow precipitate was dissolved from the filter with warm dilute ammonia (1 + 3) because the precipitate dissolves more easily at higher temperatures and because as little ammonia as possible was desired in order to avoid a large excess of ammonium chloride after neu-

¹ *Ann.*, **55**, 109 (1845).

² *Z. anal. Chem.*, **8**, 125 (1869).

³ *Ibid.*, **9**, 16 (1870).

⁴ *Ibid.*, **8**, 165 (1869).

⁵ *Ibid.*, **11**, 382 (1872).

⁶ *Ibid.*, **12**, 239 (1873).

tralization with hydrochloric acid in the manner prescribed by Fresenius. The solution was cooled after the addition of the hydrochloric acid since basic magnesium salts were precipitated from the warm solution upon the addition of the magnesia mixture. Ten cc. of magnesia mixture was added for each 0.1 gram of phosphoric acid to be precipitated. This furnished nearly twice as much magnesia as was necessary for precipitation of the phosphoric acid and the excess of magnesium salt was desired to decrease the solubility of the magnesium ammonium phosphate in the ammonia and ammonium chloride solution. After the addition of the magnesia mixture, dilute ammonia (1 + 3) was added until the volume was 100-110 cc. Standing for 3-4 hours was found sufficient for complete precipitation instead of 12 hours, as required in the directions of former authors. The precipitate was filtered off and washed as prescribed by Fresenius. No correction was applied to the weight of the magnesium pyrophosphate as this was found unnecessary. In igniting the magnesium ammonium phosphate the precipitate was first removed from the filter, which was ashed separately.

The use of magnesium chloride for the precipitation of the magnesium ammonium phosphate was not original with these authors. Brassier¹ had, in fact, recommended the use of a magnesium chloride magnesia mixture as early as 1866 but without any comment on its advantages over the magnesium sulfate magnesia mixture. Bunsen,² Rose,³ and Fresenius⁴ had also advised the use of magnesium chloride.

A further improvement was suggested by Peitzsch, Rohn and Wagner⁵ in 1880, when they recommended that the magnesia mixture be added dropwise with constant stirring rather than all at once. The filter was pierced, and the yellow precipitate was washed into a porcelain dish with 2.5 per cent ammonia. The resulting solution was poured into a beaker, and 2.5 per cent ammonia was added to bring the volume approximately to 100 cc. The magnesia mixture was then added, 15 cc. per 0.1-0.15 gram phosphoric acid (P_2O_5), without any previous addition of hydrochloric acid. The solution and precipitate were allowed to stand, while covered, for 2 hours before filtering, and the precipitate was washed with 2.5 per cent ammonia. The filter paper was dried, separated from the precipitate, and ashed upon the cover of a platinum crucible, then placed in the crucible

¹ *Ann. chim. phys.*, (4) 7, 355 (1866).

² *Z. anal. Chem.*, 10, 405 (1871).

³ *Ausführliches Handbuch der analytischen chemie*, 6th ed.

⁴ *Loc. cit.*

⁵ *Z. anal. Chem.*, 19, 444 (1880).

with the precipitate, gently heated at first, then brought to and kept at an intense glow in the flame of a Bunsen burner for 10 minutes, and finally ignited for 5 minutes over a blast lamp.

Stünkel, Wetzke and Wagner¹ modified this procedure only slightly by washing the yellow precipitate directly into the beaker and using 10 cc. of magnesia mixture for each 0.1 gram of phosphoric acid (P_2O_5). They also placed the filter in the crucible together with the magnesium ammonium phosphate precipitate, heated to char, and then continued as described by Peitzsch, Rohn and Wagner.

In the original official method of the Association of Official Agricultural Chemists² the yellow precipitate was dissolved from the filter with ammonia, and the filter was washed with hot water to give a volume of solution and washings not to exceed 100 cc. The ammonia was nearly neutralized with hydrochloric acid, the solution was allowed to cool and the magnesia mixture was added from a buret (1 drop per second) with vigorous stirring. After 15 minutes, 30 cc. of ammonia (sp. gr. 0.96) was added, and after standing at least 2 hours the precipitate was filtered off and treated as described by Stünkel, Wetzke and Wagner.

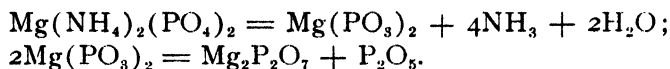
In a comprehensive study of the subject Neubauer³ showed that the composition of the magnesium ammonium phosphate precipitate obtained in the analysis of phosphates varied with the conditions under which it was formed and that changes in the conditions of precipitation were no doubt a contributing cause of the variable results frequently reported by different analysts. It was shown that the composition of the precipitate depended on the reaction of the solution and also on the ratio of magnesium to phosphoric acid at the time the precipitate was being formed. If the precipitate is formed under such conditions that the magnesia is locally in excess of the phosphoric acid, as occurs when the magnesia mixture is added all at once to an alkaline solution, high results will be obtained owing to the precipitation of some trimagnesium phosphate. If, however, the magnesia mixture is added very slowly with stirring to an alkaline solution, the phosphoric acid will then be in excess and low results will follow owing to the formation of some monomagnesium phos-

¹ *Z. anal. Chem.*, **21**, 353 (1882).

² Proceedings of the Convention of Agricultural Chemists and First Annual Meeting of the Association of Official Agricultural Chemists at Philadelphia, 1884.

³ *Z. anorg. Chem.*, **2**, 45 (1892).

phate and the subsequent loss of phosphoric acid on ignition as shown in the following equations:



The procedure of Peitzsch, Rohn and Wagner, as adopted by the Association of Official Agricultural Chemists, aims to avoid a local excess or deficiency of magnesium by recommending that the magnesia mixture be added dropwise and with stirring to a neutral or nearly neutral solution. Neubauer makes the claim, however, that best results are obtained when a slightly acid magnesia mixture is added to a solution of sufficient acidity to prevent precipitation, the phosphate then being precipitated by the slow addition of ammonia. A second precipitation is recommended.

The same procedure is also recommended by Lundell and Hoffman,¹ who confirmed the observations of Neubauer that the composition of the magnesium ammonium phosphate precipitate depends on the ratio of phosphate to magnesia at the moment the precipitate is formed, and that once the precipitate is formed its composition does not change materially on long standing at room temperature.

Attention was again called to this phase of phosphoric acid analysis in 1923 by Larison,² who pointed out that lowest results were obtained when the solution was made alkaline before precipitation with the official alkaline magnesia mixture and highest when it was made acid, and, without giving any explanation for the variations observed, concluded that the highest results were the more nearly correct. McCandless and Burton³ also reported that the reaction of the solution had a bearing on the results obtained but claimed that the addition of the magnesia mixture to a neutral solution gives best results.

These observations received the immediate attention of the Association of Official Agricultural Chemists, and a collaborative study of the subject was promptly undertaken by W. H. Ross,⁴ the Associate Referee on Phosphoric Acid. This study showed, in agreement with the work of others, that lowest results are obtained when the solutions are made alkaline prior to precipitation with magnesia mixture and highest when they are made acid, but the differences were not found to be great, and both neutral and acid solutions gave results that agreed very well with the theo-

¹ *J. Assoc. Official Agr. Chem.*, **8**, 184 (1924).

² *Ibid.*, **7**, 394 (1924).

³ *Ind. Eng. Chem.*, **16**, 1267 (1924).

⁴ *J. Assoc. Official Agr. Chem.*, **8**, 407 (1925); **9**, 182 (1926); **10**, 190 (1927).

retical. It was therefore concluded that although variations in the reaction of the solution may be a contributing source of error, it is not the principal cause of the wide variations in the results found by different analysts. Recommendations were consequently made that the official gravimetric method of the Association for the determination of phosphoric acid be retained unchanged as a routine method in the analysis of fertilizers but that the directions given for this determination be made more explicit by changing the words "nearly neutralize with strong hydrochloric acid" to read "neutralize with dilute hydrochloric acid, using bromthymol blue or litmus as indicator."

It was further concluded from results obtained in this study that failure of the magnesium ammonium phosphate to burn white is usually due to improper calcination rather than to any preceding step in the determination and that results obtained with residues that do not burn white are unreliable. It was found that magnesium ammonium phosphate precipitates that have been properly prepared and washed will readily burn to snow whiteness throughout when ignited for 1 hour at 1000° C. in an electric furnace. The recommendation was accordingly made that the words, "burn first at a low heat and then ignite intensely until white or grayish white," as given in the official gravimetric method for phosphoric acid be changed to read, "burn first at a low heat and ignite to constant weight, preferably in an electric furnace, at 950-1000° C."¹

A further possible source of error in the determination of phosphoric acid was attributed to the use of an alkaline magnesia mixture which quickly becomes contaminated through its action on the glass container. The recommendation was made that this condition be avoided by preparing neutral magnesia mixture and then adding ammonia only to that portion of the mixture required for immediate use.

In the course of this study a comparison was also made of the official gravimetric method of the Association and of other modifications of the molybdate-magnesia method as developed by Jørgensen² and by Lundell and Hoffman³ of the U. S. Bureau of Standards in their umpire method. Good results were obtained with all three methods with a slight difference in favor of the Lundell and Hoffman umpire method. This method, however, is longer than the official method of the Association, and the difference in accuracy was considered to be too small to justify its adoption in

¹ *J. Assoc. Official Agr. Chem.*, **12**, 176 (1929).

² *Analyst*, **51**, 61 (1926).

³ *J. Assoc. Official Agr. Chem.*, **8**, 184 (1924).

place of the latter for routine analysis, although it is admirably suited for umpire work.

VOLUMETRIC METHODS

The time required for a gravimetric determination of phosphoric acid has led analysts to try the speedier if less accurate processes depending on the use of volumetric methods. The chief difficulty with these methods has been the securing of combinations of constant composition and some sharp method of distinguishing the end points. In some cases, as in the uranium method, it has been necessary to remove a portion of the titrated solution and prepare it by subsidence or filtration for final testing. As is well known, this procedure for determining the end point is less accurate and more time-consuming than that depending on a change of color in the whole mass. The literature on the volumetric analysis of phosphates is extensive, and the methods proposed show a surprising range of laboratory technic and use of reagents.

These methods may be conveniently divided into two groups, according as they do or do not make use of ammonium molybdate as a precipitating agent. The methods in each of these groups may be further classified into a number of sub-groups as follows:

(a) *Methods not involving molybdate precipitation*: (1) Acidimetric and alkalimetric, (2) uranium, (3) lead, (4) silver, (5) alum, and (6) iodometric.

(b) *Methods involving molybdate precipitation*: (1) Direct titration with standard ammonium molybdate, (2) acidimetric and alkalimetric, (3) reduction, and (4) centrifugal.

The only methods of the first group that have been generally used are the uranium methods and those that involve titration with standard acid or alkali. Direct alkalimetric titration is the most rapid and accurate method for determining the concentration of high-grade phosphoric acid, and variations of this method are now generally used in the determination of free phosphoric acid in superphosphate.

Direct titration with a standard uranium solution, which has been widely used in different countries, is one of the simplest and most rapid methods for the analysis of phosphates low in iron and aluminum. The application of this method to phosphates containing iron and aluminum with the use of ammoniacal magnesium citrate, as proposed by Joulie, has also been extensive, especially in France. Directions for the determination of phosphoric acid by uranium titration are still given in such well-known publi-

cations as Sutton's "Volumetric Analysis," and Treadwell-Hall's "Analytical Chemistry," Vol. 2, but the use of this method in fertilizer laboratories has been almost entirely replaced by the acidimetric and alkalimetric methods of the group that involves precipitation with ammonium molybdate.

Direct titration with standard ammonium molybdate is of interest only because it was the first of the volumetric methods that made use of ammonium molybdate. It was immediately replaced by other methods of the group. Reduction methods, in which the ammonium phosphomolybdate precipitate is reduced with zinc and titrated with potassium permanganate, were extensively used at one time, particularly in steel laboratories, and the same is true of the Goetz centrifugal method. Directions for the zinc reduction method are still given in popular texts on quantitative analysis, such as Blair's "The Chemical Analysis of Iron," and Scott's "Standard Methods of Chemical Analysis." This method, however, like the uranium method, has been replaced in fertilizer laboratories by the acidimetric and alkalimetric methods as first proposed independently by Pemberton, Thilo and Handy, and later modified by Kilgore and other members of the Association of Official Agricultural Chemists. This modified method has been adopted as the official volumetric method of the Association of Official Agricultural Chemists, and it is also the approved method for the volumetric analysis of phosphates in all English-speaking countries. The same method, with slight alteration, is also in use in the United States Bureau of Standards, as well as in other laboratories throughout the world.

VOLUMETRIC METHODS—(a) *Not Involving Molybdate Precipitation*

Acidimetric and Alkalimetric Methods.—The methods of this group are based on the tribasic character of phosphoric acid, that is, its property of combining with the alkali and alkaline earth metals to form three series of salts, known as the mono-, di- and triphosphates. The monoalkali phosphates are acid in reaction; the dialkali phosphates are slightly alkaline; and the trialkali phosphates are strongly alkaline. Monocalcium phosphate is soluble in water, giving an acid reaction like the corresponding alkali phosphates, but the di- and tricalcium phosphates are insoluble. The hydrogen-ion concentrations of dilute solutions of the principal alkali phosphates are given in Table XIII.

TABLE XIII.—pH VALUES OF DILUTE SOLUTIONS OF THE ALKALI PHOSPHATES.

Compound	pH of solution of different molar concentrations		
	0.1	0.05	0.01
NaH_2PO_4	4.5	4.6	4.9
KH_2PO_4	4.5	4.6	4.9
$\text{NH}_4\text{H}_2\text{PO}_4$	4.4	4.5	4.6
$\text{Ca}(\text{H}_2\text{PO}_4)_2$			4.4
Na_2HPO_4	8.7	8.8	8.9
K_2HPO_4	8.7	8.8	8.0
$(\text{NH}_4)_2\text{HPO}_4$	7.8	7.8	7.8
Na_3PO_4	12.2	12.0	11.7
K_3PO_4	12.2	12.0	11.7
$(\text{NH}_4)_3\text{PO}_4$	9.0	9.0	8.9

TABLE XIV.—INDICATORS USED IN VOLUMETRIC ANALYSIS.

Chemical name	Common name	Color change	pH range
Thymol sulfonphthalein	Thymol blue	Red - yellow	1.2 - 2.8
Tetrabromphenol sulfonphthalein	Bromphenol blue	Yellow - blue	3.0 - 4.6
Parabenzene sulfonic acid azodi-methyl aniline	Methyl orange	Orange red - yellow	3.1 - 4.4
Orthocarboxybenzene azodimethyl aniline	Methyl red	Red - yellow	4.4 - 6.0
(Mixture)	Litmus	Red - blue	4.5 - 8.3
(Mixture)	Cochineal	Yellow - lilac	4.8 - 6.2
Alizarin sulfonic acid	Alizarin red	Yellow - pink	5.0 - 6.8
Dibromorthocresol sulfonphthalein	Bromcresol purple	Yellow - purple	5.2 - 6.8
Dibromthymol sulfonphthalein	Bromthymol blue	Yellow - blue	6.0 - 7.6
Phenol sulfonphthalein	Phenol red	Yellow - red	6.8 - 8.4
(Mixture)	Rosolic acid (Corallin)	Yellow - red	6.9 - 8.0
Orthocresol sulfonphthalein	Cresol red	Yellow - red	7.2 - 8.8
Thymol sulfonphthalein	Thymol blue	Yellow - blue	8.0 - 9.6
Orthocresol phthalein	Cresolphthalein	Colorless - red	8.2 - 9.8
Dihydroxyphthalophenone	Phenolphthalein	Colorless - red	8.3 - 10.0

Table XIII shows that the range of the hydrogen-ion concentration of dilute solutions of the alkali phosphates between 0.1 and 0.01 *M* is within the range covered by the common indicators listed in Table XIV. In this respect, phosphoric acid differs from the mineral acids, hydrochloric, nitric, and sulfuric, which form but one salt within the pH range of the common indicators. Thus the titration curve of sulfuric acid, as determined electrometrically by Davis, Oak and Salisbury¹ (Fig. 6) shows but one inflection between pH 3 and pH 9.5. The curve also shows that when the acid is titrated with 2 molecular equivalents of alkali solution, a very slight excess of alkali will change the hydrogen-ion concentration of the solution from pH 5 to pH 8, or over almost the entire range between methyl orange and phenolphthalein.

¹ *Ind. Eng. Chem.*, **25**, 182 (1933).

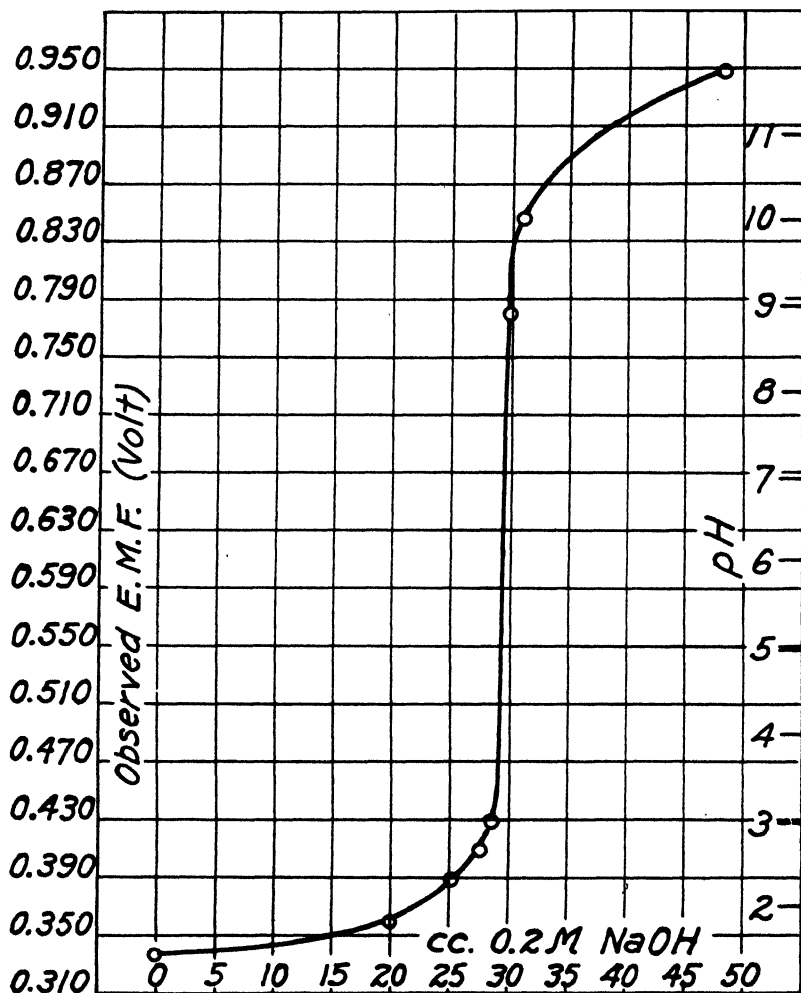


Fig. 6.—Titration of 29.8 cc. 0.1 M H_2SO_4 , Made up to 200 cc. with Conductivity Water, and Titrated with 0.2 M $NaOH$ by means of Hydrogen Electrode at 25° C.

The titration curve of phosphoric acid, on the other hand, as illustrated in Fig. 7, shows two inflections, one corresponding to the point at which the mono-salt is formed, and the other to the point at which the di-salt is formed. The first inflection point is within the pH range of methyl orange, while the second is entirely beyond the methyl orange range, but within the pH range of phenolphthalein.

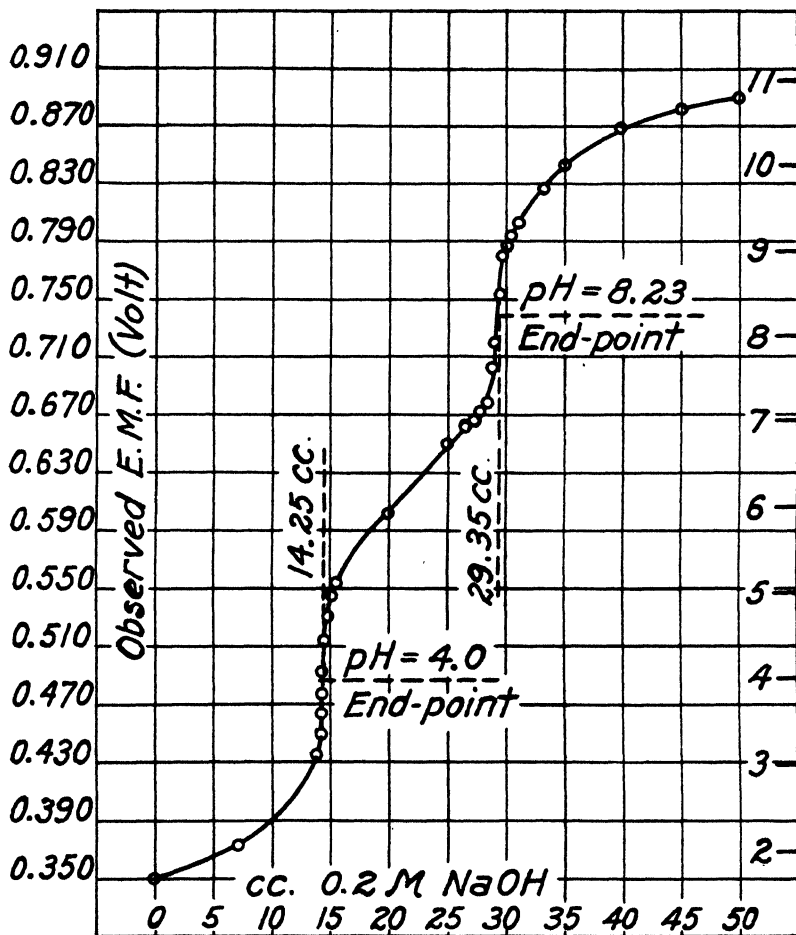


Fig. 7.—Titration of 40 cc. 0.0711 M H_3PO_4 , Made up to 200 cc. with Conductivity Water, and Titrated with 0.2 M $NaOH$, by Means of Hydrogen Electrode at $25^\circ C$.

The polybasic character of phosphoric acid thus affords a direct means of determining (1) free phosphoric acid or mixtures of alkali phosphates with or without free phosphoric acid; (2) water-soluble phosphates in superphosphates; and (3) free acid in superphosphates.

(1) *Free Phosphoric Acid and Alkali Phosphates.*—Solutions of alkali phosphates or of alkali phosphates with free phosphoric acid may be conveniently divided into two groups according as they are acid or alkaline to

phenolphthalein. The acid materials may contain any two of the three compounds—phosphoric acid, monoalkali phosphate and dialkali phosphate—while the triphosphates and other alkaline salts must be absent. Alkaline mixtures, on the other hand, consist of the di- and trialkali phosphates, with or without other alkaline compounds, such as the hydroxide or carbonate, of the alkalis. Metaphosphate may also be present.

In the procedure recommended by Smith¹ for the analysis of materials of this kind, the solution of the sample is titrated first with A cc. of normal alkali or acid to end reaction with phenolphthalein, according as the solution is initially acid or alkaline, and then with B cc. of normal acid to an end reaction with methyl orange. The solution is then further treated with an excess of B cc. of the standard acid, boiled for 30 minutes to convert metaphosphates or metaphosphoric acid into the ortho form, titrated back with B' cc. of normal alkali to an end reaction with methyl orange, and finally with C cc. more of the normal alkali to an end point as indicated with phenolphthalein. If the analysis has been properly made, the value of B' should be the same as B .

In the titration of acid materials, where A is greater than B , then $A - B = \text{H}_3\text{PO}_4$; $2B - A = \text{NaH}_2\text{PO}_4$; and $C - B = \text{NaPO}_3$ (generally nil).

If $A = B$, then each should be equal to the NaH_2PO_4 present, and if $A = 2B$, only H_3PO_4 is present.

If A were greater than $2B$, then $A - 2B$ would be a measure of the metaphosphoric acid or other acid present.

When A is less than B , $A = \text{NaH}_2\text{PO}_4$; $B - A = \text{Na}_2\text{HPO}_4$; and $B - C = \text{NaPO}_3$ (usually nil).

With alkaline salts, when no carbonate is present, and A is less than B , then $A = \text{Na}_3\text{PO}_4$ and $B - A = \text{Na}_2\text{HPO}_4$.

When C is less than B , that is, where carbonate is present, and A is less than B , then $A + C - B = \text{Na}_3\text{PO}_4$; $B - A = \text{Na}_2\text{HPO}_4$; and $B - C = \text{Na}_2\text{CO}_3$.

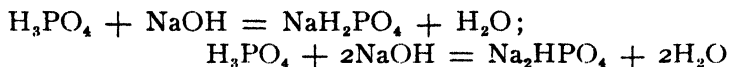
When no carbonate is present, and A is greater than B , then $B = \text{Na}_3\text{PO}_4$ and $\frac{1}{2}(A - B) = \text{NaOH}$.

When carbonate is present and A is greater than B , then $B - C = \text{Na}_2\text{CO}_3$; $C = \text{Na}_3\text{PO}_4$; and $\frac{1}{2}(A - B) = \text{NaOH}$.

In the determination of free phosphoric acid, 1 cc. of normal NaOH is equivalent to 0.098 gram of H_3PO_4 when titration is made with methyl

¹ *J. Soc. Chem. Ind.*, **36**, 415 (1917).

orange; or to one-half this quantity if made with phenolphthalein. The reactions that take place in these two titrations are as follows:

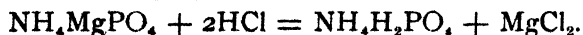


The titration with phenolphthalein is preferable in this determination because the hydrogen-ion concentration of the monoalkali phosphates is too near the alkaline end of the pH range of methyl orange for accurate reading. Dilute solutions of the dialkali phosphates give a decided pink color with phenolphthalein, and when making a titration with this indicator the addition of alkali must be continued beyond the point at which a color first appears. The end point can be most conveniently and accurately determined by matching the color with that of a solution containing approximately the same concentration of indicator and of phosphate in the form of disodium phosphate. This procedure affords the most accurate and rapid method for determining the concentration of solutions of free phosphoric acid.

(2) *Water-soluble Phosphates in Superphosphates.*—The water-soluble phosphates have the property of resisting change in reaction with the addition of acid or alkali, that is, they exert what is called a buffer effect. The end point in the titration of phosphate solutions is therefore not so sharp as in the case of solutions containing other mineral salts. It has also been observed that the inflection in the titration curve of monocalcium phosphate is less sharp and the end point therefore more difficult to discover than for the monoalkali phosphates. This condition, coupled with the precipitation of dicalcium phosphate when the alkali is added, makes the ordinary indicator titration of monocalcium phosphate of little value.

Many methods have been proposed for overcoming these difficulties, particularly in the determination of total soluble phosphates is superphosphate, by precipitating the phosphate with a neutral salt and titrating the equivalent quantity of mineral acid set free in the reaction.

One of the first of these methods, that proposed by Stolba,¹ consists in making the solution of the sample alkaline with ammonia, adding magnesia mixture, filtering, washing first with dilute ammonia and then with alcohol to remove the ammonia, dissolving in a measured excess of 0.1 *N* acid and titrating back with 0.1 *N* alkali, using carmine tincture as indicator. 1 cc. of 0.1 *N* acid is equivalent to 0.00355 gram of phosphoric acid (P_2O_5) as indicated by the following equation:



¹ *Z. anal. Chem.*, **18**, 100 (1877).

Glucksmann¹ shortened this method by treating the solution of the sample in a graduated flask with an excess of normal ammonia solution, adding sufficient neutral magnesium sulfate to precipitate the phosphate, filling to the mark, filtering, and titrating the residual ammonia in an aliquot part of the filtrate. Stolba's method was further modified by Johnson and Jenkins,² who treated the solution of the sample with a nearly saturated solution of ammonium tartrate before the addition of the magnesium mixture. The ammonium tartrate was added until the solution remained clear when slightly alkaline. This modification of the method made it applicable to the analysis of phosphates containing iron and aluminum. The magnesia mixture used in these determinations contained 70 grams of magnesium sulfate and 195 grams of ammonium chloride per liter.

In Maly's³ method the solution of phosphoric acid or alkali phosphate is placed in a flask, and a known volume of normal alkali is added in excess, A drop or two of corallin is added, and the phosphate in solution is precipitated by the addition of neutral barium chloride. The mixture is heated nearly to boiling, and the hot solution is titrated for excess acid with normal sodium hydroxide.

The method described by Clemm-Lennig⁴ is one of the oldest of the early methods for determining water-soluble phosphates in superphosphate. The aqueous solution of the superphosphate is treated with an excess of neutral calcium chloride, and the resulting solution is then titrated hot with standard sodium hydroxide, litmus being used as indicator.

Mollenda⁵ recommended precipitation of the calcium of the superphosphate instead of the acid radical by adding sodium carbonate until any further addition would produce a cloudiness and then sodium oxalate in slight excess. The filtrate was titrated with 0.2 *N* sodium hydroxide, phenolphthalein being used as indicator. Neither of these methods is applicable to the analysis of superphosphate in the presence of free acid.

In the method proposed by Emmerling⁶ use is made of a calcium chloride solution containing 200 grams per liter and a standard sodium hydroxide having a concentration equivalent to 5 grams of P_2O_5 per liter. In carrying out the method 200 cc. of the solution to be analyzed, containing 20 grams of superphosphate per liter, is mixed with 50 cc. of the calcium chloride solution. A measured volume of the standard alkali solution is

¹ *Ibid.*, **34**, 33 (1895).

² *Ann. Rpt. Conn. Agr. Expt. Sta.*, 1878, p. 117.

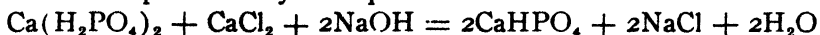
³ *Z. anal. Chem.*, **15**, 417 (1876).

⁴ *Ibid.*, **5**, 433 (1866).

⁵ *Ibid.*, **22**, 155 (1883).

⁶ *Landw. Vers.-Sta.*, **32**, 429 (1886).

transferred to a beaker, phenolphthalein and water are added, and the solution is titrated with the mixed solution of superphosphate and calcium chloride until the pink color has entirely disappeared. A second portion of the mixed solution of superphosphate and calcium chloride, equal in volume to that required in the titration, is diluted with water and then titrated with standard alkali, methyl orange being used as indicator. The volume of the standard alkali consumed in the titration with methyl orange is deducted from that obtained by titrating with phenolphthalein to give the sodium hydroxide equivalent to the total soluble phosphates in solution. The reaction involved in the titration from methyl orange to phenolphthalein is represented by the equation—

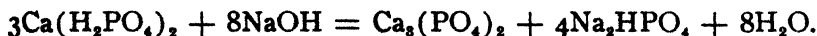


If A is the volume of standard soda solution used in the first titration, C the volume required in the second titration, B the volume of the mixed solution of superphosphate and calcium chloride used in the first titration, and T the weight of P_2O_5 equivalent to 1 cc. of the standard alkali, then X , the percentage of water-soluble P_2O_5 in the superphosphate, is given by the equation—

$$X = (A - C)T \frac{100 \times 1000 \times 250}{20 \times 200 AB}$$

This method is applicable to the determination of water-soluble phosphoric acid in superphosphates containing alkali phosphates, but not to water-soluble phosphates containing free phosphoric acid.

In the method described by Kalmann and Meisels¹ 20 grams of superphosphate is dissolved in 1 liter of water in the usual way, and 100 cc. of the clear solution is then titrated with standard 0.5 N sodium hydroxide to end points as first indicated by methyl orange and then by phenolphthalein. The reaction taking place in the titration from methyl orange to phenolphthalein is as follows:



A second 100 cc. portion of the clear solution is next transferred to a 250 cc. flask, and an excess of 0.5 N sodium hydroxide is added. The flask is filled to the mark and shaken, and the solution is filtered. An aliquot of 100 cc. of the filtrate is then titrated back with 0.5 N hydrochloric acid to an end reaction as indicated first by phenolphthalein and then by methyl orange. The number of cubic centimeters of 0.5 N hydrochloric acid required in the titration from phenolphthalein to methyl orange multiplied by

¹ *Z. angew. Chem.*, 1894, 408.

$2\frac{1}{2}$ gives the volume (B) of 0.5 N acid required per 100 cc. of the superphosphate solution. If A represents the volume of 0.5 N sodium hydroxide used in the original titration from methyl orange to phenolphthalein, then the arithmetical mean of A and B multiplied by 0.0355 gives the weight of P_2O_5 in 100 cc. of the superphosphate solution. This method is applicable to the determination of total water-soluble phosphate in superphosphates containing both alkali phosphates and free phosphoric acid.

Glaser¹ modified the volumetric method of Kalmann and Meisels so as to avoid the double titration required by the original method. In the modified method the total phosphoric acid is estimated in one operation by precipitating as the tricalcium salt, which is secured by adding at the proper time an excess of calcium chloride. The water-soluble solution of the superphosphate to be analyzed is prepared according to the official method of the Association of Official Agricultural Chemists by washing 2 grams of the sample on a filter with successive small portions of water until the filtrate measures 250 cc. A 50 cc. aliquot of the sample is titrated with 0.1 N sodium hydroxide to end reaction with methyl orange, a neutral solution of calcium chloride is added in excess, and the titration is continued to alkaline reaction with phenolphthalein. If iron and aluminum are present, a slight development of an acid reaction is produced, of which no account may be taken. Each cubic centimeter of the 0.1 N sodium hydroxide solution corresponds in the first titration to 7.1 mg. of P_2O_5 and in the second to 3.55 mg.

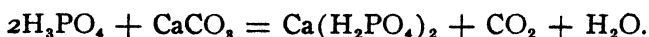
(3) *Free Acid in Superphosphate.*—The free acids that are likely to be present in superphosphate are phosphoric, sulfuric, hydrofluosilicic, and hydrofluoric, and in the ordinary course of manufacture their presence in the finished product will decrease in the order named. For many years these free acids were determined collectively in terms of sulfuric or phosphoric acid by simply titrating an aqueous solution of the superphosphate with standard sodium hydroxide to an end reaction with methyl orange.

In the titration method of the Verein Deutscher Dünger-Fabrikanten (see p. 205) 50 cc. of the solution prepared by agitating 20 grams of superphosphate in 1 liter of water is diluted with water to 300 cc. and titrated with 0.5 N sodium hydroxide, methyl orange being used as indicator. In this titration methyl orange is not considered entirely satisfactory, however, because the hydrogen-ion concentration of the monosodium phosphate formed in the reaction is too near the alkaline end of the pH

¹ *Chem. Ztg.*, 18, 1533 (1894).

range of methyl orange for most accurate reading. According to Oster-setzer¹ sodium alizarin sulfonate is a more satisfactory indicator for use in this titration. In the method that he recommends 10 grams of the superphosphate is dissolved in 400 cc. of water in a 500 cc. flask and shaken for the usual time; 4 cc. of a 5 per cent solution of sodium alizarin sulfonate is added, and the flask is filled to the mark. A 50 cc. aliquot of this solution is titrated with 0.5 *N* sodium hydroxide to the transition between yellow and brown and compared with an equal volume of the original solution to better distinguish the change of color.

In the method described by Gerhardt² calcium carbonate is used in place of sodium hydroxide as a neutralizing agent for the free acid. The reaction that takes place may be represented as follows:



In carrying out the method, 20 grams of the sample is shaken with water for 30 minutes in a liter flask; 1 gram of potassium ferrocyanide is added to precipitate the iron and aluminum and the flask is filled to the mark. To a 100 cc. aliquot of the filtrate is added an excess of a known weight of calcium carbonate, the mixture is stirred for 30 minutes, the undecomposed carbonate is filtered off and dissolved in an excess of standard acid, and the excess of acid is titrated back with standard alkali, methyl orange being used as indicator. Zockler³ reported that the error in this method due to iron and aluminum may amount to as much as 2 per cent and that it is not constant. This error, coupled with the time taken to make the determination, has prevented the general adoption of Gerhardt's method.

The methods most generally used at present for the determination of free acid in superphosphate are based on the principle of separating the free mineral acid from the other water-soluble constituents of the superphosphate by digesting with one or other of such reagents as ether, alcohol and acetone, distilling off the solvent, and determining the free acid in the residue by titration with standard alkali. This procedure not only gives a sharper end point than that shown in the direct titration method, but it also affords a means of determining the free phosphoric acid independently of the other acids present, by first titrating with an indicator having a pH range similar to methyl orange and then to end reaction with phenolphthalein. The first titration gives the sodium hydroxide equivalent of all

¹ *Chem. News*, 91, 215 (1905).

² *Chem. Ztg.*, 29, 178 (1905)

³ *Ibid.*, 29, 226, 338.

the free acids and the second that of the free phosphoric acid alone. The difference in the two readings gives the sodium hydroxide equivalent of all the free acids with the exception of phosphoric acid.

In the method proposed by Herzfelder¹ 1 gram of the finely ground sample is extracted in a Soxhlet for 10 hours with dry ether. The solvent is distilled off, the residue is treated three times with 20 cc. of water, and the liquid is passed through a filter. The paper is then washed with water just tinted with methyl orange as long as any reddening is noticeable. The filtrate is titrated with normal alkali, and the number of cubic centimeters used is multiplied by 7.1 to give the percentage of free phosphoric acid in the material. Should the quantity of alkali consumed be less than 0.5 cc., the whole operation should be repeated on a larger quantity of the sample. Guthrie and Ramsay² expressed the opinion that Herzfelder's method gives much more accurate results than that proposed by Gerhardt, but they recommended the use of sodium alizarin sulfonate as an indicator in place of methyl orange.

In the second alternative method adopted by the Verein Deutscher Dünger-Fabrikanten (see p. 205) use is made of alcohol as a solvent for the free acid of superphosphate.

According to Shuey³ acetone is equally as good if not a better solvent than alcohol for free acid in superphosphate and has the advantage that it can be easily procured in a neutral condition. It does not change appreciably in composition and therefore does not have to be neutralized before use. The acetone used for this purpose should be transparent in color, neutral in reaction, and have a specific gravity of 0.788–0.790 at 25° C. Shuey's method is as follows:

Weigh 2 grams of the material (superphosphate, acidulated base or mixed fertilizer) into a dry 100 cc. volumetric flask, fill to the mark with acetone, stopper tightly, and shake every 12 minutes for 2 hours. Filter, dilute 50 cc. of the clear solution to about 250 cc. with cold, boiled distilled water and titrate with carbonate-free 0.1 *N* sodium hydroxide, using methyl red as the first indicator. When a neutral point is reached, note the number of cubic centimeters used, add phenolphthalein, and continue the titration to the neutral point indicated by phenolphthalein.

The total titration from zero to the end point indicated by phenolphthalein represents the total free acid, while the difference between the total titration and that indicated by methyl red is equivalent to the phosphoric acid alone. The percentage of phosphoric acid, expressed as H_3PO_4 , is found by multiplying the volume of alkali required in this titration by the factor 0.9806. The difference between the

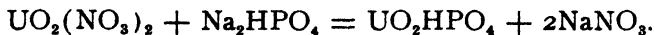
¹ *Analyst*, **28**, 372 (1903).

² *J. Proc. Roy. Soc., N. S. Wales*, **43**, 69 (1909).

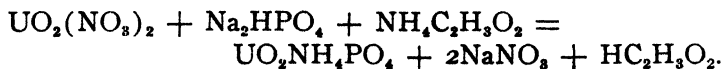
³ *Ind. Eng. Chem.*, **17**, 269 (1925).

total number of cubic centimeters used and the number required for the phosphoric acid represents the other free acids. This difference in the two titrations multiplied by the factor 0.4904 gives the percentage of these acids, expressed as H_2SO_4 .

Uranium Methods.—The uranium method as first proposed by LeConte in 1853¹ and later developed by Sutton,² Neubauer³ and Pincus⁴ is the oldest of the volumetric methods that have been in general use for the analysis of phosphates. The method is based on the fact that when uranium acetate or nitrate is added to a neutral solution of a phosphate the whole of the phosphoric acid is thrown down as a yellow uranyl phosphate.



If the solution contains free mineral acid, it must be neutralized with an alkali hydroxide, and an alkali acetate together with excess of free acetic acid should be added. If ammonium acetate is used, the phosphoric acid is precipitated as uranyl ammonium phosphate.



When fixed alkali acetates are used, instead of the ammonium salt, the precipitate consists simply of uranyl phosphate.

In the method proposed by LeConte the sample is fused with sodium carbonate and leached with water to dissolve out sodium phosphate; the filtrate is neutralized with nitric acid and made up to volume. An aliquot of the solution so prepared is then slowly added from a buret to 50 cc. of a standard uranium solution, until a small drop of the clear liquid applied with a glass rod to a porcelain plate previously moistened with a solution of potassium ferrocyanide no longer develops a reddish brown color. The standard uranium solution is prepared by dissolving 4.416 grams of uranium nitrate in a liter of water. The 50 cc. aliquot of the uranium solution is made alkaline before titrating with a few drops of potassium hydroxide solution, and dilute acetic acid is then added drop by drop to redissolve the oxide and render the solution neutral.

The procedure outlined by LeConte is not applicable to the analysis of phosphates containing any considerable quantity of iron and aluminum because analysis of such materials must be preceded by a preliminary separation of the phosphoric acid from associated impurities by precipitation

¹ *Pharm. J. Trans.*, 18, 80 (1853).

² *Volumetric Analysis*, 9th ed., p. 292, 1904.

³ *Arch. Wissenschaftliche Heilkunde*, 6, 228 (1860).

⁴ *J. prakt. Chem.*, 70, 104 (1859).

with ammoniacal magnesium citrate solution, ammonium molybdate, or other reagent. It has been found in practice that when the uranium is used the magnesium citrate separation is the most convenient. This modification of the original uranium method is known as the Joulie method.¹ Its use in France at one time was almost universal.

The details of the method are as follows:

REAGENTS

Acid sodium acetate solution.—Dissolve 100 grams of sodium acetate in water, add 50 cc. of glacial acetic acid, and make up to 1 liter.

Citro-magnesium solution.—Add 27 grams of pure magnesium carbonate by degrees to a solution of 270 grams of citric acid in 350 cc. of warm water, cool, add 400 cc. of a 10 per cent ammonia solution or sufficient to insure a decided excess of ammonia, dilute to 1 liter, and preserve in a well-stoppered bottle.

Standard monoammonium phosphate.—Dissolve 8.10 grams of the pure dry salt in 1 liter. (See p. 183). 1 cc. of this solution contains 0.005 gram of P_2O_5 .

Potassium ferrocyanide solution.—Dissolve 10 grams of the pure crystals in 100 cc. of water.

Standard uranium nitrate solution.—Dissolve about 40 grams of the pure crystals in 800 cc. of water, add a few drops of ammonia to produce a slight turbidity, then acetic acid until clear, and dilute to 1 liter. Standardize this solution as follows:

Transfer 10 cc. of the standard ammonium phosphate solution to a beaker, add 5 cc. of the sodium acetate solution, make up with water to about 75 cc., and heat to boiling. Titrate the solution with the uranium solution until a drop of the liquid deposited on a white plate no longer assumes a brownish-red color when a glass rod moistened with the potassium ferrocyanide solution is brought in contact with it. The removal of several drops involves some error in the titration, and when this is done repeat the titration by adding merely the required volume of the uranium solution, as shown by the preceding titre. Before any portion of it is withdrawn for testing, verify the end point by adding three or four drops of the uranium solution in excess and test again, when a strongly marked color should be produced. Run a blank titration with 5 cc. of the sodium acetate. Dilute to 75 cc. with boiling water and apply the proper correction. The strength of the standard uranium solution should be verified at intervals in common with other standard solutions for use in volumetric work.

DETERMINATION

If organic matter is present incinerate the sample before analysis, because it interferes with the use of uranium as a reagent. Dissolve 1-10 grams of the ignited residue, or of the original sample in the absence of organic matter, in hydrochloric acid, or if pyrite is present, in hydrochloric and a little nitric acid. Boil the sample with the acid in a volumetric flask until the residue is perfectly white. Cool, and make up to volume. (The removal of silica by evaporation to dryness is necessary only in those cases where the sample contains silicate decomposable by

¹ *Mon. sci.*, 2 (3), 212-32, 531-47 (1872); *Ann. Agron.*, 11, 97-129 (1855).

hydrochloric acid with separation of gelatinous silica.) Filter, or allow to settle, withdraw an aliquot corresponding to 50 mg. of P_2O_5 , and add 10 cc. of the citromagnesium solution and a large excess of ammonia. If a precipitate forms immediately, it is iron or aluminum phosphate. In this case, discard the first aliquot and withdraw a second. Add 20 cc. of the citromagnesium solution, allow to stand 2-12 hours, filter, and wash by decantation and on the filter with dilute ammonia until the filtrate gives no precipitate with a disodium phosphate solution. Dissolve the precipitate in the beaker and on the filter with dilute nitric acid and wash with dilute nitric acid into a 150 cc. beaker. Add dilute ammonia until a slight turbidity is produced, clarify with 1 or 2 drops of dilute nitric acid, heat to boiling, add 5 cc. of sodium acetate solution, and titrate with the standard uranium solution as described in the standardization of that solution.

The solution of the sample in nitric acid changes any arsenic present to arsenic acid, which reacts in the uranium method of analysis in the same way as phosphoric acid and therefore gives high results if any considerable amount is present. This cause of error may be avoided by passing sulfur dioxide through the solution, bringing it to the boiling point to drive off excess of sulfur dioxide, and afterwards precipitating the arsenic with hydrogen sulfide. After filtration, the rest of the operation can be carried on as already described.

The acetic acid solution of a calcium phosphate may deposit dicalcium phosphate on boiling. Fresenius, Neubauer and Luck¹ claimed that this precipitate is a possible source of error in the uranium method and recommended that the titration be made in the reverse order by adding the phosphoric acid to a boiling standard uranium solution. Schumann,² Abesser, Jani and Märcker,³ Brügelmann,⁴ and Pavec⁵ do not favor this procedure and quote experimental evidence to show that possible danger of loss of calcium phosphate may be avoided in the direct titration by adding the greater part of the standard uranium before heating the solution to boiling.

Abesser, Jani and Märcker also recommend the use of calcium phosphate of known P_2O_5 content, as determined gravimetrically by the molybdate-magnesium method, rather than an alkali phosphate for standardizing the uranium solution.

Mohr⁶ proposed adding the potassium ferrocyanide indicator to the solution in excess of that required to precipitate the iron present and then titrating with the standard uranium solution. This procedure, however,

¹ *Z. anal. Chem.*, **10**, 147 (1871).

² *Ibid.*, **11**, 382 (1872).

³ *Ibid.*, **12**, 252 (1873).

⁴ *Ibid.*, **10**, 16 (1877).

⁵ *Ibid.*, **10**, 350 (1879).

⁶ *Chem. Ztg.*, **11**, 417 (1887)

is claimed by Reis¹ to be unsatisfactory, owing to the difficulty of determining the end point of the titration in the presence of Prussian blue.

In 1889 the *Versammlung der Chemiker an Deutschen Dünger Fabriken und der Handelschemiker*² concluded that the volumetric determination of phosphoric acid by the uranium method as commonly used was no longer reliable and up-to-date. Its use was permitted until a later date by the *Verein Deutscher Dünger Fabrikanten* for the analysis of superphosphates low in iron and aluminum, but the method has now been almost entirely replaced by other methods.

Satisfactory results are claimed by Spencer³ in a modification of Joulie's uranium method, in which the citro-magnesium solution is replaced by silver carbonate in the separation of the phosphoric acid. In the operation of this method the fertilizer is first ignited until all organic matter and residual carbons are destroyed. The residue is then dissolved in nitric acid and made up to volume. To an aliquot of the slightly acid solution containing about 0.1 gram of P_2O_5 , is added sufficient silver carbonate to saturate the free acid present and precipitate all the phosphoric acid as silver phosphate, Ag_3PO_4 . The precipitate with excess of silver carbonate is washed with hot water and dissolved in dilute nitric acid, the excess of silver is precipitated with sodium chloride, and the phosphoric acid in the filtrate is determined by means of a standard solution of uranium nitrate, as described in the Joulie method. The author claims that the separation of the phosphoric acid by the silver method is more exact than by the Joulie citro-magnesium process, but it has never been generally adopted for the analysis of fertilizers in this country.

Lead Methods.—The principle of the lead methods depends upon the fact that in aqueous and acetic solutions a lead phosphate of constant composition is precipitated on addition of a soluble lead salt. In the method originally proposed by Schwartz⁴ and Mohr⁵ the phosphoric acid is precipitated by adding an excess of standard lead nitrate solution and then titrating the excess of lead with standard potassium chromate, silver nitrate being used as indicator. When making the titration the solution must be only weakly acid, and the excess of lead must not be too great.

In the method as described by Wavelet⁶ the phosphoric acid is precipitated by magnesium citrate solution as in the Joulie uranium method, and

¹ *Z. angew. Chem.*, 1888, 354.

² *Ibid.*, 1889, 690.

³ 8th Ann. Rpt. Purdue University, 1882, p. 240.

⁴ *Dinglers Polytech. J.*, 1859, 264 (1863).

⁵ *Z. anal. Chem.*, 2, 253 (1863).

⁶ *Répert. pharm.*, 40, 153 (1893).

the washing of the precipitate and its solution in nitric acid is also conducted as in that method. The phosphoric acid is then titrated with standard lead nitrate directly, potassium iodide being used as indicator. The reagents required in the process are as follows:

(1) A 5 per cent sodium nitrate solution; (2) standard lead nitrate solution; and (3) 5 per cent potassium iodide solution. In the analysis of raw phosphates, 5 grams of material is dissolved in dilute nitric acid, and the solution is made up to 250 cc. An aliquot of 50 cc. is withdrawn and made alkaline with ammonia, and 10 cc. of the citro-magnesium solution is added to precipitate magnesium ammonium phosphate. The precipitate is filtered, washed with dilute ammonia, and dissolved in dilute nitric acid. The resulting solution is made slightly alkaline with ammonia, acidified with dilute acetic acid, and made up to 200 cc. To a 50 cc. aliquot of this solution is added 5 cc. of sodium acetate, and the solution is titrated at room temperature with the standard lead nitrate solution, potassium iodide being used as indicator. The end reaction is determined by placing a drop of the titrated mixture on a white plate in contact with a drop of potassium iodide solution. When all the phosphoric acid is precipitated, the least excess of lead salt is revealed by the characteristic yellow precipitate of lead iodide.

The author of the process claims that the lead phosphate is insoluble in the excess of acetic acid and that the phosphate itself does not give any yellow coloration with potassium iodide. The process is considered to be quite as exact as the uranium method, and the end reaction is sharper. In common with the uranium method, it has now been replaced by other methods in the analysis of fertilizer materials.

Silver Methods.—In the silver nitrate method proposed by Perrot¹ an excess of 0.1 *N* silver nitrate solution is added to an acetic acid solution of the phosphate to be analyzed, and the excess of silver is determined by the Volhard thiocyanate titration. This method was investigated by Spencer,² who found the process unreliable. Fairly satisfactory results were obtained, however, by a modification of the process. The principle of this method depends on the separation of the phosphoric acid by silver carbonate and subsequent titration with standard uranium solution, after the removal of the excess of silver. Spencer's method may thus be considered a modification of Joulie's uranium method, in which the citro-magnesium solution is replaced by silver carbonate in the separation of the

¹ *Compt. rend.*, **83**, 495 (1881).

² *Loc. cit.*

phosphoric acid. The details of this method are therefore described under the heading of "Uranium Methods." (See p. 166).

In the modification of Perrot's method as proposed by Clark¹ the phosphate is dissolved in water, nitric acid or sulfuric acid; the greater proportion of the free acid is neutralized with caustic soda; and a solution of sodium acetate containing free acetic acid is added in excess. If the addition of the acetate produces a precipitate, this must be filtered off, redissolved and reprecipitated with sodium acetate as before and the filtrate and washings added to the previous filtrate. An excess of silver nitrate is added to precipitate silver phosphate, and the free acetic acid is neutralized with caustic soda until there is only a faint acid reaction to litmus paper. The slightest excess of alkali will cause a brown precipitate of silver oxide, but this readily dissolves on the addition of a few drops of dilute acetic acid. The precipitate of silver phosphate, which will contain any chloride that may be present, is thoroughly washed with water and dissolved on the filter with dilute nitric acid; a little ferric sulfate is added to the filtrate, and the phosphoric acid is determined by the Volhard method of titrating with standard sodium thiocyanate. The precipitate of iron and aluminum phosphates is dried, ignited, weighed and dissolved in acid, and the iron is determined volumetrically and calculated to iron phosphate. The balance is assumed to be aluminum phosphate.

The method proposed by Holleman² is similar to that suggested by Perrot in that the phosphoric acid is precipitated with an excess of silver nitrate, and the excess is determined by the Volhard method.

In the operation of the method, 50 cc. of the solution to be analyzed, containing a slight excess of nitric acid and not more than 0.2 gram of P_2O_5 , is treated with 10 cc. of normal sodium acetate solution, and a slight excess of 0.1 *N* silver nitrate is added. The solution is neutralized with 0.1 *N* sodium hydroxide, the quantity required having been previously determined by titrating 10 cc. of the liquid to be analyzed, and phenolphthalein is used as indicator. Five times the quantity required for neutralization of the 10 cc. less 0.5 cc. is added. By this treatment the phosphoric acid is completely precipitated as silver phosphate.



The excess of silver in the filtrate is determined by titrating an aliquot with ammonium thiocyanate, ferric potassium alum being used as indicator. The presence of sulfuric and nitric acids does not interfere with the reac-

¹ *J. Soc. Chem. Ind.*, 7, 311 (1888).

² *Z. anal. Chem.*, 23, 185 (1894).

tion, but hydrochloric acid must be absent. Alkali and alkaline earth metals may be present, but not the heavy metals.

When iron and aluminum are present, 100 cc. of the solution is precipitated with 30 cc. of normal sodium acetate, and the phosphoric acid is determined volumetrically in 50 cc. of the filtrate. The precipitate of iron and aluminum phosphates is weighed and ignited, and its weight multiplied by 0.2225 is added to the P_2O_5 found volumetrically.

Inasmuch as most commercial phosphates contain iron and aluminum, and it is necessary to determine them gravimetrically, there would seem to be little or no gain in time and no simplification of the process to analyze such material by a volumetric method of this kind.

Alum Methods.—Methods involving precipitation as aluminum phosphate have long been used for the gravimetric determination of phosphorus and particularly of aluminum. Attempts have been made to apply the same principles in the volumetric analysis of phosphorus, but none of the methods proposed is sufficiently promising to warrant its adoption in the analysis of fertilizers. In the oldest of these methods (Fleischer's¹), an acetic acid solution of the phosphate is titrated with 0.1 *N* alum solution until no further precipitation occurs, as indicated by testing small drops of the filtrate.

In Spica's method² the sample of phosphate to be analyzed is heated with sulfuric acid until the latter is almost entirely driven off, and the residue is treated for the recovery of phosphoric acid by leaching with absolute alcohol. The resulting solution is evaporated to drive off alcohol; neutralized with sodium hydroxide, as indicated with phenolphthalein; and made up to volume. An aliquot is titrated with a standard solution of ferric ammonium alum until a violet color shows with salicylic acid. Iron, aluminum and manganese must be absent. The alum solution may be standardized against a solution of microcosmic salt containing 2.9439 grams per liter, of which 1 cc. is equivalent to 0.001 gram of P_2O_5 . Arnold and Wedemeyer³ investigated this method, but they could not recommend it because alcohol is not a satisfactory separating agent and the results are too low when it is used.

¹ *Z. anal. Chem.*, 4, 19 (1865).

² *Gazz. Chim.*, (1) 22, 117 (1892).

³ *Z. angew. Chem.*, 1892, 603.

Iodometric Methods.—The method of Christensen¹ is based on the reaction that takes place between free acid and a mixture of potassium iodide and potassium bromate, as represented in the following equation:



In the analysis of free phosphoric acid by this method, a solution of the sample containing not more than 0.5 gram of phosphoric acid is treated with 10 cc. of a 5 per cent potassium bromate solution and 3 grams of potassium iodide is added. The resulting solution is diluted to 100–120 cc., allowed to stand on a water bath at 40–50 C. for 30 minutes, cooled and titrated with 0.1 *N* sodium thiosulfate solution. 1 cc. of 0.1 *N* sodium thiosulfate solution is equivalent to 0.0071 gram of P_2O_5 .

In applying the method to the analysis of an insoluble phosphate such as basic slag, the sample is treated with citric acid and the phosphoric acid in solution is precipitated as ammonium magnesium phosphate in the usual way. The precipitate is washed first with 2.5 per cent ammonia, then with alcohol to remove ammonia, and dissolved in an excess of standard sulfuric acid, at least 30 cc. of 0.1 *N* sulfuric acid being used for this purpose for each 0.1 gram of P_2O_5 in the precipitate. The reaction involved in the solution of the precipitate is as follows:



The analysis is completed by adding potassium iodide and potassium bromate and titrating with 0.1 *N* sodium thiosulfate as described for free phosphoric acid.

The equation shows that 3 mols of dibasic sulfuric acid are replaced in the reaction with 2 mols of phosphoric acid, which is claimed to act in the liberation of iodine as a monobasic acid. Two equivalents of acid are thus lost in the reaction for each equivalent of phosphoric acid that is formed. The sodium thiosulfate equivalent to the phosphoric acid in the magnesium ammonium phosphate precipitate is therefore obtained by subtracting the cubic centimeters of the thiosulfate solution required in the titration from the volume equivalent to the 0.1 *N* sulfuric acid used in dissolving the precipitate and dividing the result by 2. 1 cc. of 0.1 *N* sodium thiosulfate solution as before is equal to 0.0071 gram of P_2O_5 .

Jørgensen² considers the method unreliable owing to the possible liberation of iodine by the monopotassium phosphate formed in the reaction.

¹ *Z. anal. Chem.*, **36**, 81-94 (1897).

² *Mem. acad. roy. sci. letters, Denmark*, 7th ser., **2**, No. 4, 176 (1905).

In the method proposed by Lindeman and Motteu¹ the phosphoric acid is precipitated as manganous ammonium phosphate and determined indirectly by iodometric titration of the manganese in this precipitate. The solution of alkali phosphate to be analyzed is treated with ammonia, ammonium chloride and ammonium citrate solutions, and sufficient manganous sulfate is added to precipitate the phosphoric acid as manganous ammonium phosphate. The precipitate is washed, dissolved in hydrochloric acid, treated with hydrogen peroxide, made alkaline with potassium hydroxide, boiled, cooled and acidified with hydrochloric acid; an excess of potassium iodide is added; and the iodine set free is titrated with a standard solution of sodium thiosulfate. The reactions involved in the successive steps of the determination may be represented as follows:

(1) $\text{MnNH}_4\text{PO}_4 + 3\text{HCl} = \text{MnCl}_2 + \text{NH}_4\text{Cl} + \text{H}_3\text{PO}_4$; (2) $\text{MnCl}_2 + \text{H}_2\text{O}_2 + 2\text{HCl} = \text{MnCl}_4 + 2\text{H}_2\text{O}$; (3) $\text{MnCl}_4 + 2\text{KI} = \text{MnCl}_2 + 2\text{KCl} + \text{I}_2$; and (4) $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$.

The claim is made that only 5/6 of the manganous salt is oxidized to the manganic form by treatment with hydrogen peroxide and that 10 mols of the sodium thiosulfate is therefore equivalent to 3 mols of P_2O_5 .

Insoluble phosphates are analyzed by dissolving in nitric acid, precipitating with ammonium molybdate, dissolving in ammonia, and proceeding as described for the analysis of alkali phosphates. The method is obviously too long and is not sufficiently accurate to justify its use in the analysis of fertilizers.

VOLUMETRIC METHODS—(b) *Involving Molybdate Precipitation*

Direct Titration with Standard Molybdate Solution.—The use of ammonium phosphomolybdate in the direct titration of phosphoric acid was first proposed by Pemberton in 1882.² The method consisted in adding ammonium nitrate to a nitric acid solution of the phosphate, neutralizing with ammonia, heating to 60°C. or above, and then titrating with a standard solution of ammonium molybdate until, after the settling of the precipitate, further addition of the standard solution produced no cloudiness in the clear liquid. The standard solution was prepared by dissolving 89.543 grams of ammonium molybdate in water and making up to a liter. One cc. of this solution corresponds to 0.003 gram of P_2O_5 . If necessary to secure a clear solution, the addition of a little ammonia before filling to the liter mark was recommended.

¹ *Bull. soc. chim.*, 13 (3), 523-33 (1895).

² *J. Frank. Inst.*, 112, 184-93 (1882).

Similar methods have also been described by Hundeshagen,¹ Grete² and Arragon.³ An outline of the Pemberton method was included in a report that was presented to the Association of Official Agricultural Chemists at its second meeting in 1884. The method proved to be tedious and uncertain owing to the difficulty of determining the end point, and it was quickly replaced by more convenient methods involving the use of ammonium molybdate.

Acidimetric and Alkalimetric Methods.—The analysis of phosphates by titration of the ammonium phosphomolybdate precipitate with caustic alkali was first suggested by Pemberton in 1882 at the time he announced his direct titration method. The details of the method were not published, however, until 1893. In the meantime a number of other chemists described methods for determining phosphoric acid by the same general procedure of dissolving the molybdate in an excess of standard alkali and titrating back with standard acid.

This general method of analysis was first described in detail by Thilo,⁴ who applied it to the determination of phosphoric acid in basic slag. From 2 to 2.5 grams of the sample is dissolved in hydrochloric acid and heated to boiling with the addition of a little nitric acid to oxidize the iron. The solution is cooled and made up to volume, and an aliquot corresponding to 0.25 gram of the sample is treated with ammonia until a precipitate forms. The solution is acidified with nitric acid in slight excess, warmed to 70° C., 50 cc. of ammonium molybdate solution is added, and the solution is stirred for 5 minutes to precipitate ammonium phosphomolybdate. The precipitate is filtered, washed with 20 per cent ammonium nitrate solution and dissolved in an excess of standard ammonia solution, and the excess of ammonia is titrated with standard sulfuric acid, litmus being used as indicator. The ammonia solution is standardized against a weighed amount of pure, dry ammonium phosphomolybdate, prepared by treating a solution of sodium phosphate with an excess of the molybdate solution. The molybdate solution recommended by Thilo for this determination contained 5 parts of molybdic acid, 15 of ammonia, and 75 of nitric acid per 100 cc.

A method described by Isbert and Stutzer⁵ for the analysis of phosphates differs from that described by Thilo in that phosphoric acid is determined

¹ *Chem. News*, 60, 202 (1889).

² *Ber.*, 21, 2762 (1888).

³ *Rev. gen. chim.*, 6, 9 (1903).

⁴ *Chem. Ztg.*, 11, 193 (1887).

⁵ *Z. anal. Chem.*, 26, 583 (1887).

indirectly from the ammonia content of the ammonium phosphomolybdate precipitate. The sample is dissolved in aqua regia, filtered, and an excess of ammonia is added to a suitable aliquot of the filtrate. The resulting solution is acidified with nitric acid, and the P_2O_5 is precipitated with molybdate solution at 60° - 70° C. The precipitate is washed with cold water, transferred with the filter to an Erlenmeyer flask, sodium hydroxide is added in excess, and the ammonia is distilled off into a solution of standard acid which is then titrated back with standard barium hydroxide solution, rosolic acid being used as indicator. Reis,¹ Hundeshagen¹ and Laible² claim that this method is not accurate because the ammonia content of the molybdate is not constant.

An extensive investigation of various methods of determining phosphoric acid by use of ammonium molybdate was made by Hundeshagen in 1889.³ He showed that the yellow precipitate formed on adding ammonium molybdate to a solution of the phosphate has the composition $-(MoO_3)_{12}PO_4(NH_4)_3-$ when freed from molybdic acid and other impurities, and that 23 mols of alkali are required to neutralize one mol of ammonium phosphomolybdate. In applying the alkalimetric titration of this compound to the volumetric analysis of phosphates, it is recommended that the precipitate be washed with 5 per cent ammonium nitrate, an excess of standard sodium hydroxide added, and the excess of alkali titrated with standard nitric acid, phenolphthalein being used as indicator.

In the method proposed by Manby⁴ for the determination of phosphorus in iron and steel, the phosphate in solution is precipitated near the boiling point with molybdate solution. The precipitate is washed with a solution containing 3 per cent each of nitric acid and potassium nitrate, dissolved in 50 per cent ammonium hydroxide, the excess ammonia is boiled off and 2 cc. of nitric acid (sp. gr. 1.20) is added. The solution is again evaporated to dryness, heated to expel nitric acid and ammonium nitrate, and the residue is dissolved in an excess of standard sodium hydroxide. The excess of alkali is finally titrated with standard nitric acid as described by Hundeshagen. The molybdate solution used in making the precipitation is prepared by dissolving 100 grams of molybdic oxide in 150 cc. of water and 100 cc. of concentrated ammonia, the excess of ammonia is allowed to distil off, and the residue is poured into 1500 cc. of dilute nitric acid (1 + 2).

¹ *Loc. cit.*

² *Chem. Z.*, **11**, 286 (1887).

³ *Z. anal. Chem.*, **28**, 171 (1889); *Chem. News.*, **60**, 168, 177, 188, 201, 215 (1889).

⁴ *J. Anal. Applied Chem.*, **6**, 82 (1892).

Handy¹ showed that the steps in Manby's method of evaporating to dryness and heating to expel nitric acid and ammonium nitrate were unnecessary and that the time required to make a determination could be greatly reduced by washing the precipitate first with 1 per cent nitric acid and then with 0.1 per cent potassium nitrate solution, dissolving the precipitate in an excess of standard sodium hydroxide, and titrating with standard nitric acid in the usual way. A similar procedure was also recommended by Rothberg and Auchinvole.²

As stated previously Pemberton made a preliminary announcement of an alkalimetric method for phosphate analysis in 1882, the details of which were not published until 1893. This method,³ which was intended particularly for the analysis of phosphate rock and phosphatic fertilizers, received the immediate attention of the Association of Official Agricultural Chemists, and the following year it formed the subject of a collaborative study of the Association under the direction of B. W. Kilgore, Referee on Phosphoric Acid. The method as submitted by the collaborators in this preliminary study was as follows:

REAGENTS

Ammonium molybdate.—Dissolve 90 grams of crystallized ammonium molybdate in somewhat less than a liter of water, filter, and make up to the mark.

Standard potassium hydroxide solution.—Dilute 323.8 cc. of normal potassium hydroxide to 1 liter. 1 cc. of this solution is equivalent to 1 mg. of P_2O_5 .

Standard acid solution.—Prepare a hydrochloric or nitric acid solution having the same strength volume for volume as the standard potassium hydroxide solution.

Phenolphthalein indicator.—Dissolve 1 gram of phenolphthalein in 100 cc. of 60 per cent alcohol.

DETERMINATION

Dissolve 1 gram of phosphate rock or 2-3 grams of fertilizer in nitric acid and, without evaporating to dryness, dilute to 250 cc. Transfer an aliquot of 25 cc. to a 150 cc. beaker, add ammonia until a precipitate just begins to form, and then treat with 5 cc. of nitric acid (sp. gr. 1.4). Add 10 cc. of a saturated solution of ammonium nitrate, dilute to 50-75 cc., heat to boiling, add sufficient ammonium molybdate solution to insure complete precipitation, and filter at once. Thoroughly wash the precipitate by decantation and on the filter, transfer filter and precipitate to the beaker in which the precipitation has been made, dissolve the precipitate in an excess of the standard alkali, and add at least 0.5 cc. of phenolphthalein solution and then standard acid until the color disappears.

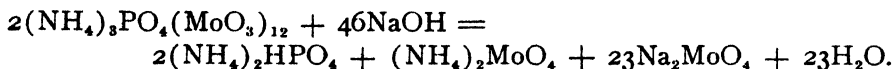
¹ *J. Anal. Applied Chem.*, 6, 204 (1892).

² *Ibid.*, 243.

³ *J. Am. Chem. Soc.*, 15, 382 (1893).

The use of phenolphthalein as indicator was recommended because it had been shown by Long¹ to give accurate results in the presence of the limited quantity of ammonium salts contained in the solution, provided the solution is cold and the indicator is used in sufficient quantity.

The reaction involved in the solution of the ammonium phosphomolybdate precipitate in the standard sodium hydroxide solution is represented by the following equation:



In this equation, 46 mols of sodium hydroxide are equivalent to 1 mol of P_2O_5 , and 1 cc. of 0.1 N sodium hydroxide solution neutralizes an equivalent of 0.3089 mg. of P_2O_5 in the molybdate precipitate.

The reports submitted in this first collaborative study of the method were on the whole favorable, although the results obtained were somewhat more variable than those obtained with the official gravimetric method. A tendency towards high results was also noted.

In a report submitted to the Association the same year Kilgore² showed that more concordant results could be obtained by introducing certain modifications in the method. The more important of these modifications included a change in the temperature at which precipitation is made from near boiling to 45°-50° C., and in the strength of the molybdate solution from 66 grams of molybdic acid (MoO_3) per liter to 50 grams, as in the official reagent for use in gravimetric analyses. It was further recommended that the molybdate solution be acidified, before using, with 5 cc. of strong nitric acid per 100 cc. These modifications were included in the collaborative study that was made of the method during 1895 and the following year the further modification was introduced of washing the molybdate precipitate with cold water rather than with dilute solutions of nitric acid and potassium nitrate.³ The work was continued for two more years, when the method was adopted as an optional method for the determination of phosphoric acid. The referee's report for 1898 also made reference to tests on a further modification of the method which consisted in precipitating at room temperature with continuous stirring rather than at 45°-50° C. with occasional shaking. A favorable report on this modification of the volumetric method was made to the Association

¹ *Am. Chem. J.*, **11**, 84 (1889).

² U. S. Dept. Agr. Bur. Chem. Bull., **47** 100-4 (1895).

³ *Ibid.*, **40**, 60 (1897).

two years later by Williams.¹ This report and the satisfactory results obtained in the collaborative studies of the modified procedure resulted in its adoption in 1900 as an alternative step in the optional volumetric method for determining phosphoric acid. The last of these referee's reports, which were presented in 1901 and 1903, gave results on a comparative study of this method with the gravimetric method.²

Although no further report was presented to the Association for a period of 25 years, numerous papers on the subject appeared in the literature during this time. These publications showed that the method had not been entirely reliable under all conditions and that slight deviations from the accepted procedure materially affect the results.³ The presence of sulfates in particular was found to be a disturbing factor, giving high results when precipitation is made at 45°-50° C., as in the more commonly used procedure of analysis. This was first pointed out by Richardson,⁴ who recommended the elimination of sulfates by the addition of an equivalent amount of barium chloride solution immediately following the acid digestion of the sample, cooling, making up to volume, and filtering in the usual way. It was shown that the high results obtained in the presence of sulfates was due to a complex ammonium sulfomolybdate which has the acid nature of ammonium phosphomolybdate and which is simultaneously formed when phosphoric acid is precipitated by ammonium molybdate. This was later confirmed by Falk and Suguira,⁵ who expressed the view that the ammonium sulfomolybdate combination is an essential part of the phosphomolybdate precipitate. The preliminary removal of sulfates by the addition of a barium salt has also been recommended by Breckenridge.⁶

Shuey⁷ has shown that the presence of sulfates does not interfere and that their removal is unnecessary if precipitation is made at 20°-30° C. with stirring as in the alternative official volumetric method. A similar conclusion was also reached by Bible⁸ in a comparative study of the two procedures.

In view of these observations a collaborative study of the official volumetric methods was again undertaken in 1928 and in 1929. The results

¹ U. S. Dept. Agr. Bur. Chem. Bull., 62, 55 (1900).

² *Ibid.*, 67, 22 (1902); 61, 163 (1904).

³ Cf. Carpenter, *J. Ind. Eng. Chem.*, 2, 157 (1910).

⁴ *J. Am. Chem. Soc.*, 29, 1314 (1907).

⁵ *J. Am. Chem. Soc.*, 37, 1307 (1915).

⁶ *Ind. Eng. Chem.*, 16, 1180 (1924).

⁷ *Ibid.*, 9, 367 (1917).

⁸ *J. Assoc. Official Agr. Chem.*, 11, 126 (1928).

showed, in agreement with previous work on the subject, that the presence of sulfates seriously interferes with the volumetric analysis of phosphates when precipitation is made at 45°-50° C., but that the interference is slight when precipitation is made at 25°-30° C. with continuous stirring. It was pointed out that laboratory temperatures vary greatly in different sections at different seasons of the year and that the expression "room temperature" as given in the alternative volumetric method is not sufficiently definite. It was accordingly recommended that the wording "room temperature" in this method be changed to read "25°-30° C." and that the procedure of precipitating at 45°-50° C. with occasional shaking be stated as not applicable to the volumetric determination of phosphoric acid in the presence of sulfates.



Fig 8 — Ross, Kershaw Stirring Apparatus

A convenient stirring apparatus for use in the official method for determining phosphoric acid is shown in Fig. 8. This apparatus differs from others of a similar type in that the solution is stirred with a straight glass rod. The rod can be easily and quickly attached to the spring clamp provided for holding it in place and as easily withdrawn for subsequent use in filtering the solution. A single belt suffices to drive all the stirring rods.

Fig. 9 shows a shaking machine adapted for use with Erlenmeyer flasks. The circular plate holding the flasks is given a combined eccentric and tilting motion which brings about an efficient agitation of the solution in the flasks without danger of loss through splashing. The flasks are

supported on the plate by spring clamps and can be removed or replaced while the apparatus is in motion. Either machine may be operated by a one-tenth horsepower motor.



Fig 9 —Ross Kershaw Shaking Machine

Neumann¹ has proposed a modification of the Pemberton method that is particularly adapted to the determination of phosphoric acid in organic materials. The sample for analysis, containing not more than 0.05 gram of P_2O_5 , is digested in a mixture of equal parts of concentrated sulfuric and nitric acids until organic matter is destroyed, diluted with 40 cc. of water, and 25 grams of ammonium nitrate is added. If more than 40 cc. of the acid mixture is used in the digestion, the ammonium nitrate taken and the volume of the solution should be proportionately increased. The solution is then heated to 70° - 80° C., and the phosphoric acid is precipitated by adding ammonium molybdate, shaking for 30 seconds and allowing to stand for 15 minutes. The precipitate is washed on a filter with ice cold water, transferred with the filter to the flask in which the precipitation has been made, and 150 cc. of water is added. The filter is broken up by shaking, and the precipitate is dissolved in an excess of 0.5 *N* potassium hydroxide. The solution is then boiled until all ammonia is dispelled, and cooled, and the excess of alkali is titrated with 0.5 *N* sulfuric acid, phenolphthalein being used as indicator.

¹ *Z. physik. Chem.*, **37**, 115 (1902).

In the reaction that takes place under these conditions between potassium hydroxide and the ammonium phosphomolybdate precipitate, 56 mols of the standard alkali are required for each mol of P_2O_5 present. One cc. of the 0.5 *N* potassium hydroxide solution therefore corresponds to 1.268 mg. of P_2O_5 .

Reduction Methods.—The use of a reduction method in the volumetric determination of phosphoric acid was first suggested by Sopp¹ in 1858. This method has been the subject of many subsequent investigations, and is one of the oldest of the volumetric methods for the determination of phosphoric acid. It is an indirect method as applied to this determination in that it specifies precipitating the phosphoric acid as ammonium phosphomolybdate, filtering, dissolving in ammonia, reducing the molybdic acid to a lower state of oxidation by means of zinc and sulfuric acid, and then titrating the reduced oxide with a standard solution of potassium permanganate.

A similar method was later developed independently by Wright,² who applied the principle used by Werncke³ for the volumetric determination of molybdic acid to the determination of phosphorus in the ammonium phosphomolybdate precipitate. The method was later modified by Emmerton,⁴ Drown,⁵ Jones,⁶ Dudley and Pease,⁷ Noyes and Frohman,⁸ Noyes and Royse⁹ and others. Inasmuch as Emmerton was the first to publish a detailed investigation of the method in the United States, it has frequently been referred to in this country as the Emmerton method.

The method as perfected by these investigations is particularly adapted to the determination of phosphorus in iron and steel and is the best known of the volumetric methods in use for this purpose. The results obtained with it are considered to be very accurate when the details are carefully observed. This method was adopted by the subcommittee appointed by the International Steel Standards Committee of the United States to consider all the rapid methods for the determination of phosphorus in iron and steel. The details of the method as approved by this committee are as follows:

¹ *Landw. Mitt.*, **1**, 62 (1858).

² *Trans. Am. Inst. Min. Eng.*, **10**, 197-200 (1881).

³ *Z. anal. Chem.*, **14**, 1 (1875).

⁴ *Trans. Am. Inst. Min. Eng.*, **15**, 93-102 (1886).

⁵ *Ibid.*, **18**, 90 (1889).

⁶ *Ibid.*, 705.

⁷ *J. Anal. Applied Chem.*, **7**, 108 (1893); *J. Am. Chem. Soc.*, **15**, 519 (1893); **16**, 224 (1894).

⁸ *J. Am. Chem. Soc.*, **16**, 553 (1894).

⁹ *Ibid.*, **17**, 129 (1895).

REAGENTS

Dilute sulfuric acid solution.—Dilute 25 cc. of concentrated sulfuric acid to 1 liter to give a 2.5 per cent solution by volume.

Potassium permanganate solution.—Dissolve 12.5-15.0 grams of crystallized potassium permanganate in 1 liter of water and filter through asbestos.

Ammonium molybdate solution.—Dissolve 100 grams of molybdic oxide in 400 cc. of ammonia (sp. gr. 0.96) and pour the solution slowly, with constant stirring, into a mixture of 400 cc. of strong nitric acid (sp. gr. 1.42) and 600 cc. of water. Add 1 cc. of a 10 per cent solution of sodium phosphate, stir vigorously, and allow to stand in a warm place for 18 hours; filter before using.

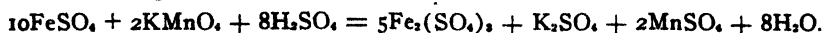
Acid ammonium sulfate solution.—To 1 liter of water add 15 cc. of strong ammonia (sp. gr. 0.90) and 25 cc. of strong sulfuric acid (sp. gr. 1.84).

Amalgamated zinc.—Dissolve 5 grams of mercury in 25 cc. of dilute nitric acid (1 + 1); dilute to 150 cc. and transfer to a flask of about 1000 cc. capacity. Pour into it 500 grams of 20-30 mesh granulated zinc. Shake thoroughly and pour off the solution; wash the zinc thoroughly with water, dry, and preserve in a glass-stoppered flask.

Ferric alum.—Dissolve 200 grams of ferric ammonium sulfate crystals in 1950 cc. of water. Add 50 cc. of sulfuric acid (sp. gr. 1.84) and 80 cc. of phosphoric acid (85 per cent).

Standard potassium permanganate solution.—Dissolve 3.0-3.2 grams of crystallized potassium permanganate in 1 liter of water. Filter it through asbestos and store in a dark-colored bottle. Standardize the solution by one of the following methods:

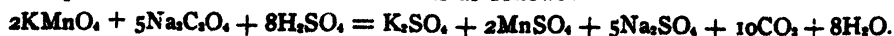
(1) Dissolve from 0.15 to 0.25 gram of pure iron in 40 cc. of dilute sulfuric acid (1 + 3); add sufficient potassium permanganate to oxidize the iron and carbonaceous matter, avoiding an excess; cool; add 10 cc. of dilute ammonia (1 + 1); pass through a Jones reductor, as in the reduction method described below for the determination of phosphorus; and titrate with the permanganate solution. The reaction that takes place is as follows:



To determine the normality of the permanganate solution, multiply the weight of the iron wire taken by the percentage of iron in the wire, divide it by the number of cubic centimeters of potassium permanganate solution used and multiply the result by the factor $\frac{1000}{5584}$.

(2) Dissolve in nitric acid a definite weight of iron, containing a known quantity of phosphorus, and determine the value of the permanganate solution in terms of the phosphorus present by precipitating with ammonium molybdate, dissolving in ammonia, reducing the molybdic acid with a Jones reductor, and titrating in exactly the same way as in the reduction method described below for the determination of phosphorus.

(3) Prepare a 0.1 N solution of sodium oxalate, containing 0.67 gram per 100 cc.; dilute an aliquot of 25 cc. to 100 cc.; acidify with 10 cc. of dilute sulfuric acid (1 + 4); heat to 70° C. and titrate with the permanganate solution to a faint permanent pink color. The reaction involved is as follows:



The normality of the potassium permanganate solution is given by dividing the product 25×0.1 by the number of cubic centimeters of the permanganate solution required in the titration. Sodium oxalate can be obtained from the U. S. Bureau of Standards with a guarantee of purity. When this salt is available the standardization of potassium permanganate against this reagent is recommended as most accurate and convenient.

APPARATUS.

Jones reductor.—This is shown in Fig. 10. It consists of a tube, *A*, 1.8 cm. inside diameter and 30 cm. long. The small tube below the contraction with the stopcock *B* is 0.6 cm. inside diameter and should reach almost to the bottom of the receiving flask *C*. A flat piece of fine platinum gauze, or a perforated porcelain plate, *D*, is placed at the point of the contraction and on top of this is placed in turn a plug of glass wool, *E*, about 1 cm. thick, and a coating of asbestos, *F*, not over 1 mm. thick. The tube is then filled with amalgamated zinc *G*, as shown in the figure. A pressure regulator, *H*, may be conveniently used to regulate the pressure in the flask *C* by adjusting the depth of the glass tube, *I*, in the water or other liquid contained within the regulator.

DETERMINATION

Weigh 1–2 grams of steel drillings or other material to be analyzed into a 250 cc. Erlenmeyer flask. Add 100 cc. of nitric acid (sp. gr. 1.135), cover with a watch-glass, and heat until the solution is complete and nitric acid is boiled off. Add 10 cc. of strong potassium permanganate solution and boil until the pink color has disappeared and manganese dioxide has separated. Add a small crystal of ferrous sulfate and repeat the addition of sulfate until the precipitated manganese dioxide is redissolved. Boil 2 minutes longer, cool, add dilute ammonia (1 + 1) until the iron is entirely precipitated and then dilute nitric acid cautiously with stirring until the solution just becomes clear again; adjust to a temperature of about 65° C., add 40 cc. of molybdate solution, shake for 5 minutes, filter and wash with acid ammonium sulfate until 2 or 3 cc. of the wash water gives no reaction for molybdenum with a drop of ammonium sulfide. Dissolve the precipitate on the filter with 5 cc. of strong ammonia (sp. gr. 0.96) in 20 cc. of water and wash with hot water into the flask to a volume of about 60 cc.; add 10 cc. of strong sulfuric acid and pass the solution through the Jones reductor into a flask containing 50 cc. of ferric alum solution; rinse the flask with dilute sulfuric acid and transfer to the funnel of the reductor when it is nearly empty in such a way as to wash it; follow with 200 cc. more of warm, dilute acid, and finally with 50 cc. of hot water. In no case allow the funnel to get empty. Close the stopcock *B* when there is still a little of the wash water in the funnel above the zinc in order to prevent access of air. Titrate the recovered solution with the standard permanganate until it assumes a faint pink color which remains for a minute. Make a blank determination by passing through the reductor a solution containing a mixture of 10 cc. of strong sulfuric acid, 10 cc. of dilute ammonia and 50 cc. of water, followed by 200 cc. of dilute sulfuric acid as described above. Subtract the titre secured in the blank titration from the volume required to titrate the reduced solution. Multiply the number of cubic centimeters thus obtained by the value of 1 cc. in terms of phosphorus, multi-

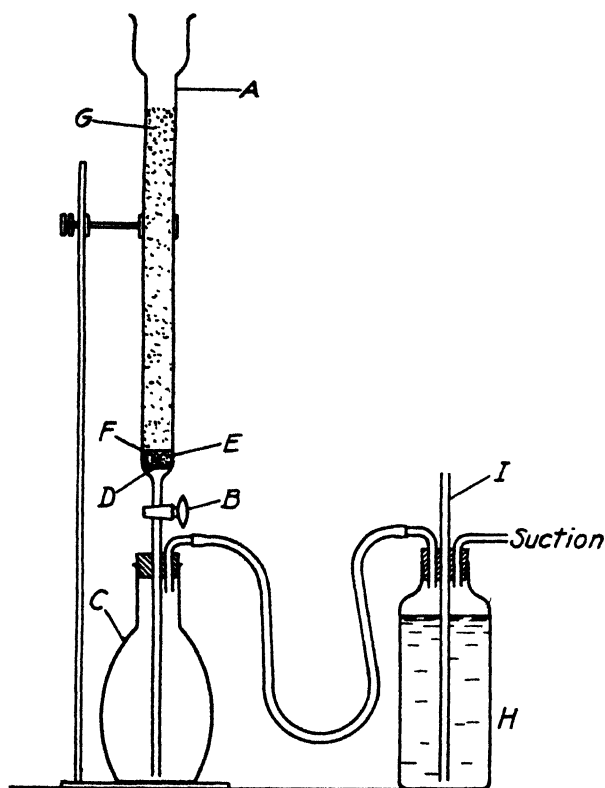


Fig. 10.— Jones Reductor.

ply this product by 100 and divide by the weight taken in order to obtain the percentage of phosphorus in the sample. The amount of permanganate required to give the blank a distinct color should not exceed 0.2–0.3 cc.

The molybdenum is entirely reduced in passing through the reductor to the form Mo_2O_3 and is oxidized by the ferric alum to the form MoO_3 , an equivalent amount of iron being reduced to the ferrous condition. One cc. of 0.1 *N* potassium permanganate is equivalent under these conditions to 0.1972 mg. of P_2O_5 . If the ferric alum solution is not placed in the flask a slight oxidation takes place before titration, the oxide $\text{Mo}_{24}\text{O}_{37}$ apparently being formed.¹ The value of 1 cc. of 0.1 *N* potassium permanganate when the titration is made in this way is then equivalent to 0.2030 gram of P_2O_5 .

¹ Blair, *Chemical Analysis of Iron*, 7th ed., p. 96.

In the use of the Jones reductor, care should be taken to exclude air from the zinc by keeping it continuously covered with water. If the apparatus is left standing for a time it is important that the zinc be washed with hot, dilute sulfuric acid and water before it is used. The reductor should be so arranged that the whole reduction occupies but 2 or 3 minutes.

In a modification of the method proposed by Campbell¹ the molybdate solution is reduced with stannous chloride to molybdenum pentachloride. The latter is then oxidized with an excess of a known amount of potassium bichromate, and the excess is determined by means of ferric chloride, the spot method with potassium ferrocyanide being used as indicator. The excess of stannous chloride is removed with mercuric chloride.

Fairbanks² developed a method for determining phosphorus in iron by reducing the ammonium phosphomolybdate precipitate with potassium iodide in hydrochloric acid, neutralizing with sodium bicarbonate and titrating with standard iodine solution.

Centrifugal Methods.—The centrifugal methods for the determination of phosphoric acid are based on the direct measurement of the volume occupied by the ammonium phosphomolybdate precipitate. This procedure was first proposed by Sopp in 1858,³ and later applied by Eggertz to the determination of phosphorus in iron and iron ores. The Eggertz method consists in treating a nitric acid solution of the sample with ammonium molybdate, stirring for 2–3 hours at 40° C., transferring the precipitate to a small graduated tube, compressing the precipitate in the tube and noting its apparent volume. The tube had an internal diameter of 1 mm. and was provided with a funnel at one end; the other end was closed with a cotton plug covered with filter paper to permit the escape of excess liquid. The tube was so graduated that each division corresponded to 0.01 per cent of phosphorus on the basis of a 1 gram sample.

The use of a centrifugal for collecting the precipitates in a graduated tube was first suggested by Goetz, manager of the Otis Steel Company, Cleveland, Ohio, in a communication to a former professor.⁴ The method was further modified two years later by Bormann,⁵ who adapted the method to the analysis of high carbon steels by treating the solution of the

¹ *J. Anal. Chem.*, **2**, 370 (1887).

² *Z. anorg. Chem.*, **13**, 117 (1897).

³ *Loc. cit.*

⁴ Wedding, *Stahl und Eisen*, **1887**, 118.

⁵ *Z. angew. Chem.*, **1889**, 638.

sample with potassium permanganate to oxidize the carbon that would otherwise be deposited and add to the bulk of the molybdate precipitate.

In carrying out the method as thus developed, 1.2 grams of the sample is dissolved in 15 cc. of nitric acid ($1 + 1$) and boiled 2 minutes, and 10 cc. of a 25 per cent solution of ammonium nitrate is added. The resulting solution is transferred while still hot to a pear-shaped tube with a graduated prolong of standard internal diameter, 30 cc. of ammonium molybdate solution is added, and the volume of the solution is adjusted to a proper height by the addition of ammonium nitrate solution. The vessel is then stoppered, shaken vigorously 1 minute, placed in a centrifuge, and rotated for 2 minutes at a speed of 12,000 r.p.m. A reading is then made of the apparent volume of the yellow precipitate that collects in the prolong of the tube.

In the case of high carbon steels, the sample is dissolved in 25 cc. of nitric acid ($9 + 1$), the solution is concentrated to small volume, and 8–12 drops of a 0.12 per cent potassium permanganate solution are added. The manganese dioxide that separates out is dissolved in 5–10 drops of concentrated hydrochloric acid, the solution is again concentrated to expel excess hydrochloric acid, 10 cc. of ammonium nitrate solution is added, and the process is continued as before.

The compact precipitate that collects in the prolong of the tube during the centrifuging process may be readily removed at the end of a determination by inverting the tube and directing a fine stream of water into the precipitate from a supply stored at a higher level.

The ammonium molybdate solution used in this determination may be prepared by dissolving 100 grams of molybdic oxide in 415 cc. of dilute ammonia (144 cc. of strong ammonia in 271 cc. of water), filtering, and pouring the filtrate slowly with stirring into 1637 cc. of dilute nitric acid (489 cc. of strong nitric acid in 1148 cc. of water).

Graduated tubes which are specially designed for this determination may now be obtained from chemical supply houses under the trade name of "Goetz tubes." Specially designed centrifuges having aluminum arms fitted with conical aluminum holders for the Goetz tubes are also available.

A standard Goetz tube as shown in Fig. 11 has a capacity of about 100 cc. The upper part of the tube has an internal diameter of about 60 mm., while that of the graduated portion is about 2.5 mm. The graduated part of the tube is about 40 mm. long and has a capacity of 0.2 cc. It is divided into 40 equal parts of 5 cu. mm. each. The capacity of each division is such that the quantity of precipitate required to fill it after centrifuging

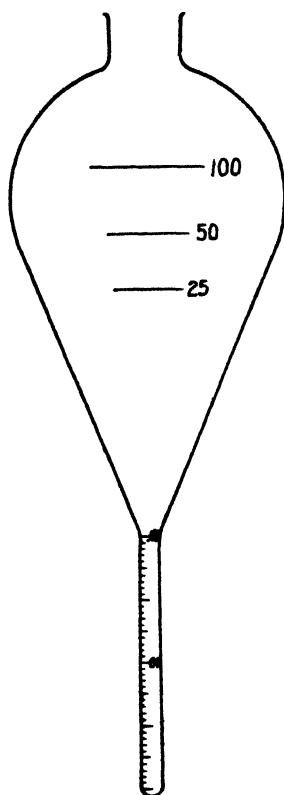


Fig. 11.—Goetz Tube.

corresponds to 0.01 per cent of phosphorus on the basis of a 1.2 gram sample. The reading on the scale thus gives the phosphorus directly expressed in hundredths of 1 per cent.

This method, which is commonly referred to as the Goetz method, has long been used as a rapid control method in the manufacture of steel, but is now being replaced by methods involving the alkalimetric titration of the yellow precipitate.

STANDARDS FOR THE DETERMINATION OF PHOSPHORIC ACID

A common practice among many authors of methods for the determination of phosphoric acid has been to check the accuracy of the proposed method against a standard material whose composition is determined by other methods of analysis. This procedure is open to the objection that

the assumed composition of the standard is subject to the error involved in its analysis.

A similar criticism is to be made of the frequent use of such a standard as sodium ammonium phosphate or disodium phosphate, whose phosphoric acid content is assumed to be known independently of any method of analysis. Each of the salts mentioned is unstable and is likely to undergo partial decomposition in the process of drying. The assumed composition of a sample of either of these materials is therefore also subject to error and it is very probable that much of the controversy that has taken place over methods of phosphoric acid analysis has been due to the use of standards of uncertain composition.

It is possible, however, to prepare standard phosphates which have a phosphoric acid content that can be estimated with a high degree of accuracy independently of any methods of analysis. These phosphates are monoammonium phosphate and monopotassium phosphate.

Monoammonium phosphate does not contain any water of hydration, and it may be safely dried to constant weight at 105° – 110° C. It crystallizes readily, forming large well-defined tetragonal crystals which are among the least hygroscopic of soluble materials. It may be prepared in a high state of purity by adding ammonia to a solution of crystallized phosphoric acid until it reacts alkaline to methyl orange and acid to methyl red. The crystallized salt that separates on concentrating the solution, if necessary, and cooling is recrystallized two or three times, dried at 110° C., and ground in an agate mortar.

Monopotassium phosphate is isomorphous with monoammonium phosphate and may be prepared in a corresponding way by adding pure potassium carbonate to a solution of crystallized phosphoric acid. The crystallized salt contains no water of hydration and may be safely dried at 110° C. without decomposition. This salt is now prepared commercially in a high state of purity for use as a buffer in hydrogen-ion work. Like monoammonium phosphate, it is one of the least hygroscopic of soluble salts. Its composition may be checked by noting the loss of weight on igniting the dry salt. The orthophosphate is thereby changed to the metaphosphate with a decrease in weight of 13.23 per cent.

The most carefully analyzed phosphatic material for which records are available is the phosphate rock standard sample No. 56 of the U. S. Bureau of Standards. The accuracy of the value assigned to this sample for its percentage of phosphoric acid has been confirmed by numerous analysts using different methods and by use as a standard in collaborative studies of

the Association of Official Agricultural Chemists. The assigned P_2O_5 content of this sample and the theoretical values for the ammonium and potassium phosphates are as follows:

Material	Phosphoric acid (P_2O_5)
	Per cent
Monoammonium phosphate	61.72
Monopotassium phosphate	52.18
Standard phosphate rock sample No. 56	31.33

Standards having a lower phosphoric acid content than the values given may be readily prepared by mixing one or other of these samples with the desired weight of dry potassium sulfate. This salt is not hygroscopic, does not contain water of hydration and can be readily dried without decomposition.

Certain insoluble materials may also be used as diluents in the preparation of lower grade standards, but owing to the acid nature of ammonium and potassium phosphates it is important that the mixture does not include calcium carbonate or other readily decomposable compounds.

OFFICIAL METHODS

The following specific methods for the determination of phosphoric acid in fertilizer materials and mixed fertilizers are considered official or have been legally prescribed as official in different countries.

UNITED STATES

The methods official in the United States are those of the Association of Official Agricultural Chemists. They are published by the Association in *Methods of Analysis, A.O.A.C.*

GREAT BRITAIN¹

TOTAL PHOSPHORIC ACID

I REAGENTS

(a) *Molybdic acid solution*.—125 grams of molybdic acid and 100 cc. of water shall be placed in a liter flask, and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 cc. of 8 per cent ammonia solution, prepared as described under (c). 400 grams of ammonium nitrate shall be added, the solution shall be made up to the mark with water and the whole added to 1 liter of nitric acid (sp. gr. 1.19). The solution shall be maintained at about 35° C. for 24 hours and then filtered.

¹ Statutory Rules and Orders No. 421, 14 (1928).

(b) *Magnesia mixture*.—110 grams of crystallized magnesium chloride and 140 grams of ammonium chloride shall be dissolved in 1,300 cc. of water. This solution shall be mixed with 700 cc. of 8 per cent ammonia solution, and the whole shall be allowed to stand for not less than 3 days and shall then be filtered.

(c) *Ammonia solutions*.—One volume of ammonia solution of specific gravity 0.880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution or water as required until the specific gravity of the solution is 0.967.

The 2 per cent ammonia solution shall be prepared as follows:—

One volume of 8 per cent ammonia solution shall be mixed with three volumes of water.

2 Preparation of Solution

(A) A weighed portion of the sample shall be heated with concentrated sulfuric acid until all organic matter is destroyed and the phosphoric acid is completely in solution. After dilution the solution shall be filtered, the insoluble matter thoroughly washed, and the filtrate made up to a definite bulk. The phosphoric acid shall be determined by the method prescribed in par. 3, in an aliquot part of the solution, which shall first be nearly neutralized and then acidified with nitric acid. The insoluble matter is to be washed from the filter and re-extracted with acid, and any phosphoric acid present in the solution shall be added to the main quantity.

(B) *Alternative method*.—A weighed portion of the sample shall be incinerated or otherwise treated to destroy organic matter, if present. When direct incineration is employed, the weighed portion of the sample shall be treated, before being heated, with a nitrate or other oxidizing material to prevent loss of phosphoric acid during heating or subsequent treatment. The residue (or the weighed portion taken, if no organic matter is present) shall be dissolved in hydrochloric acid, with the addition, if necessary, of nitric acid, and the solution shall be evaporated to dryness, or, if much calcium is present, to a sirupy consistency to fix silica. The residue shall be boiled with nitric acid and, when much iron is present, with hydrochloric acid also. After dilution the solution shall be filtered, the insoluble matter thoroughly washed and the filtrate made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the method prescribed in par. 3. The insoluble matter is to be washed from the filter and reextracted with acid, and any phosphoric acid present in the solution shall be added to the main quantity.

3 DETERMINATION

To the solution, under 2, which should contain not more than 0.4 gram of phosphoric acid (P_2O_5), and preferably from 0.1 to 0.3 gram, 100-150 cc. of molybdic acid solution, or an excess of such solution, *i. e.*, more than is sufficient to precipitate all the phosphoric acid present in the solution, shall be added, and the vessel containing the solution shall be placed in a water bath maintained at 70° C. for 15 minutes, or until the solution has reached 70° C. It shall then be taken out of the bath and allowed to cool, and the solution shall be filtered, the phosphomolybdate precipitate being washed several times by decantation and finally on the paper with 1 per cent nitric acid solution. The filtrate and washings shall be mixed with more

molybdic acid solution and allowed to stand for some hours in a warm place in order to ascertain that the whole of the phosphoric acid has been precipitated. The phosphomolybdate precipitate shall be dissolved in cold 2 per cent ammonium solution and about 100 cc. of the ammonia solution shall be used for the solution and washings. The solution shall be raised to the boiling point, the beaker removed from the burner, and 15-20 cc. of magnesia mixture, or an excess of such mixture, i. e., more than sufficient to precipitate all the phosphoric acid present, shall then be added drop by drop, with constant stirring. The stirring shall be continued at intervals so long as the liquid remains very warm. After standing at least 4 hours with occasional stirring, the precipitate shall be filtered off, washed with 2 per cent ammonia solution until free from chloride, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings should not exceed 200 cc., and are to be tested by the addition of more magnesia mixture.

WATER-SOLUBLE PHOSPHORIC ACID

4 REAGENT

Ammonium citrate solution.—110 grams of pure citric acid shall be dissolved in water, the solution treated with 400 cc. of 24 per cent ammonia (sp. gr. 0.9135) and then diluted to 1 liter.

5 PREPARATION OF SOLUTION

Twenty grams of the sample shall be continuously agitated for 30 minutes in a liter flask with 800 cc. of water at room temperature. The flask shall then be filled to the mark and shaken, and the contents shall be filtered.

6 DETERMINATION

(A) 50 cc. of the filtrate under 5 shall be boiled with 20 cc. of concentrated nitric acid, and the phosphoric acid shall be determined by the molybdate method prescribed in par. 3. In the case of fertilizers in which the proportion of phosphoric acid soluble in water is small, a larger quantity of the filtrate prepared as above shall be taken.

(B) *Alternative method.*—50 cc. of the filtrate under 5 shall be boiled with 20 cc. of concentrated nitric acid and cooled, and the excess of acid shall be neutralized with ammonia; 50 cc. of ammonium citrate solution shall be added and the mixture raised to the boiling point. Magnesia mixture shall then be added in the manner prescribed in par. 3.

CITRIC-ACID SOLUBLE PHOSPHORIC ACID

7 PREPARATION OF SOLUTION

Five grams of the sample shall be transferred to a stoppered bottle of about 1 liter capacity; 10 grams of pure crystallized citric acid shall be dissolved in water, the volume shall be made up to 500 cc., and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 cc. of alcohol, or methylated spirit, before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 cc. instead of 500 cc. The bottle

shall be at once fitted into a mechanical shaking apparatus and shall be continuously agitated during 30 minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper.

8 DETERMINATION

Fifty cubic centimeters of the filtrate under 7, shall be taken, and the phosphoric acid shall be determined by the molybdate-magnesium method prescribed in par. 3.

9 INSOLUBLE PHOSPHORIC ACID

The quantity of water-soluble phosphoric acid, as determined in par. 6, shall be deducted from the quantity of total phosphoric acid, as determined in par. 3, and the difference, if any, shall be taken as the quantity of insoluble phosphoric acid.

The methods described for Great Britain are official also for Ireland¹ and New Zealand.² The methods in use in Canada and India³ are essentially the same as those adopted as official by the Association of Official Agricultural Chemists.

GERMANY

*Verband Landwirtschaftlicher Versuchs-Stationen im Deutschen Reiche*⁴

TOTAL PHOSPHORIC ACID

I PREPARATION OF SOLUTION

(a) *Raw phosphates*.—In case of raw phosphates and other substances not containing disturbing quantities of organic matter, moisten 5 grams with some water and then heat with not more than 50 cc. of concentrated sulfuric acid, frequently shaking, until completely decomposed. (Solution in sulfuric acid with the addition of nitric acid is also permissible, the nitric acid being for the most part boiled off again.) Dilute with water, bring the cloudy solution to 500 cc. after it has cooled, and filter. Do not consider the volume of the undissolved matter. Determine the phosphoric acid in the filtrate by the Lorenz molybdate method, as directed under 14, p. 201, using 10 cc. of the filtrate, equivalent to 0.1 gram of material.

(b) *Guanos, bone meals, and fish meals*.—Bone meals, guanos, fish meals and other substances with rather large quantities of organic matter are best dissolved by the Kjeldahl procedure, with the addition of mercury, in order to determine both nitrogen and phosphoric acid. To obtain a reliable average sample in the case

¹ Statutory Rules and Orders No. 146, 8-10 (1910).

² New Zealand Gazette, No. 72, 2917 8 (1928).

³ Agr. Research Inst., Pusa, Bull., 164, 2, (1926).

⁴ Landw. Vers.-Sta., 89, 337 (1917).

of raw bone meal, fish guano and similar materials, take 10 grams and determine the phosphoric acid by the Lorenz molybdate method, as directed under 14, p. 201, or by the citrate method as directed under 5, p. 199.

Shortly before filling to the mark add 1 cc. of saturated sodium chloride solution¹ to precipitate the mercurous ions when determining phosphoric acid by the citrate method. (Solution in sulfuric acid with the addition of some strong nitric acid, which is for the most part again boiled off, is also permissible. Too much sulfuric acid should not be used for the Lorenz molybdate and citrate methods. In the Lorenz molybdate method the solution should contain about 1 cc. of concentrated sulfuric acid and in the citrate method it must be considered that the quantity of ammonia contained in 100 cc. of ammonium citrate solution, produced without any loss of ammonia, neutralizes 15.9 grams, equivalent to 8.6 cc. of concentrated sulfuric acid.)

(c) *Thomas phosphate meals*.—Moisten 10 grams with some water and heat with 50 cc. of concentrated sulfuric acid until completely decomposed. Add water before the solution is completely cool, shake the hot solution sufficiently to disintegrate any crusts present, cool, and dilute to 500 cc., disregarding the insoluble matter. Do not wait too long before filling to the mark and mixing, otherwise it will be difficult to distribute uniformly the more concentrated solution enveloped by the precipitate. Determine the phosphoric acid in 50 cc. of the solution by the citrate method, as directed under 5, p. 199, but use 100 cc. of the ammonium citrate solution instead of 50 cc. Since complete precipitation is obtained with more difficulty than in the case of superphosphate solutions, stir or shake vigorously and take care especially that the citrate solution does not have too small an ammonia content.

2 REAGENTS

(a) *Sulfate-molybdate solution*.—Pour 4500 cc. of nitric acid (sp. gr. $1.40 \frac{15^\circ}{15^\circ}$) over 500 grams of ammonium sulfate contained in a 10 liter cylinder which is not too narrow, or in a bottle with a wide mouth and a mark at 10 liters volume, and stir with a strong glass rod. (Complete solution of the salt is unnecessary.) Pour about 4 liters of boiling hot water over 1500 grams of comminuted ammonium molybdate in a porcelain dish. (The molybdate dissolves very quickly on stirring.) Cool the solution to room temperature, pour a thin stream into the ammonium sulfate-nitric acid mixture while stirring, cool, fill to 10 liters with water, mix, filter, and preserve the finished reagent in a glass-stoppered, brown glass bottle in a dark, cool place. Let stand about 2 days to separate any possible phosphoric acid in the reagents.

(b) *Nitric acid, sp. gr. $1.20 \frac{15^\circ}{15^\circ}$ (1.19-1.21)*.—Nitric acid of this concentration is a customary article of commerce. It can be made by mixing 500 cc. of nitric acid (sp. gr. 1.40) with 700 cc. of water.

(c) *Nitric acid, containing sulfuric acid*.—Pour 30 cc. of sulfuric acid (sp. gr. $1.84 \frac{15^\circ}{15^\circ}$) into 1 liter of nitric acid (sp. gr. $1.20 \frac{15^\circ}{15^\circ}$, 1.19-1.21) and mix.

(d) *Two per cent aqueous solution of pure ammonium nitrate*.—If the solution does not have a slightly acid reaction, acidify very slightly with nitric acid.

¹ *Z. angew. Chem.*, 1894, 678.

(c) *Acetone*.—The ordinary commercial *Acetonum purissimum* is satisfactory. It should be kept in brown glass bottles. Chemically pure acetone boils at 56.3° C. and has a density of $0.7971 \frac{15^{\circ}}{4^{\circ}}$. Acetone to be used in the Lorenz molybdate method must give a clear mixture with an equal volume of water, have a neutral reaction, contain no fractions boiling above 60° C., and satisfy the following tests for the absence of appreciable quantities of water, ammonia and aldehyde. The acetone must at most give only a very pale blue color to dehydrated copper sulfate upon shaking, otherwise it must be shaken with potassium carbonate and then redistilled. A moistened strip of red litmus paper held in place by the stopper of the acetone bottle and hanging in the space above the acetone must not turn blue in the course of some time, otherwise the acetone must be shaken with finely powdered oxalic acid and redistilled. To test for aldehyde, heat 10 cc. of acetone¹ with 5 cc. of ammoniacal silver solution for 15 minutes in a water oven. The liquid must not assume a brownish color.

To recover the acetone easily collect it separately in filtering, receive in a brown glass bottle, and distil, using a good still head; owing to its inflammability, avoid doing the distillation over an open flame. (The fractions passing over from 55° to 60° C. are again usable as wash fluid if they are sufficiently free from water.) Discard the fractions below 55° C. Collect the residues at 60° C. in a brown glass bottle and add potassium carbonate to extract the water. Separate the aqueous layer and repeat the procedure until the potassium carbonate does not completely dissolve. Pour off the acetone, shake with finely powdered oxalic acid until it has a slightly acid reaction in order to combine with the ammonia which forms from the ammonium nitrate, and filter. Then distil the filtrate as described above. Discard the residue from this distillation.

3 DETERMINATION

(Lorenz Molybdate Method)

Proceed as described under 14, p. 201.

4 REAGENTS

(a) *Ammonium citrate solution*.—Make a citric acid solution containing 800 grams of crystallized citric acid in 1 liter. To 1.25 liters of this solution in a 10 liter bottle add about 4 liters of water and 3.5 liters of ammonia (sp. gr. $0.91 \frac{15^{\circ}}{15^{\circ}}$). After cooling bring the volume to 10 liters with water. (The addition of the ammonia should be made slowly and with cooling so that loss of ammonia is avoided as much as possible. Too small an ammonia content is a source of error.) A citrate solution, produced and stored without loss of ammonia, contains 100 grams of crystallized citric acid and 7.96 grams of total ammonia, equivalent to 6.55 grams of nitrogen per liter. Of this quantity 5.53 grams, equivalent to 4.54 grams of nitrogen, is free ammonia. To test, dilute 25 cc. of the ammonium citrate solution (preferably measured in a volumetric flask) to 1 liter and use 50 cc. for an ammonia determination. This quantity (50 cc.) corresponds to 1.25 cc. of the original citrate solution. In case all losses have been avoided, it should contain 0.0818 gram of ammoniacal nitrogen.

¹ Merck's Chemical Reagents, Their Purity and Tests, Merck & Co., New York, 1914, p. 1.

(b) *Magnesia mixture*.—Dissolve 550 grams of crystallized magnesium chloride, 700 grams of ammonium chloride, and 2.5 liters of ammonia (sp. gr. $0.96 \frac{15^{\circ}}{15^{\circ}}$) in water to a volume of 10 liters. If it is considered desirable, use the non-hygroscopic double salt, magnesium ammonium chloride, instead of the deliquescent magnesium chloride, as proposed by Loges,¹ with a corresponding decrease in the quantity of ammonium chloride. As a matter of precaution test the magnesium content of the double salt.

5 DETERMINATION

(Citrate Method)

To 50 cc. of solution prepared as directed under 1 (b) or 1 (c), and equivalent to 1 gram of material, add 50 cc. of ammonium citrate solution and then 25 cc. of magnesia mixture. Add the magnesia mixture quickly and mix the solution at once by stirring or shaking. Stir or shake 30 minutes to separate the precipitate completely and continue the determination as directed under 5, p. 199.

6 WATER-SOLUBLE PHOSPHORIC ACID

Place 20 grams of superphosphate in a Stohmann liter flask (Fig. 12) or 10 grams in a Stohmann half-liter flask, fill to the mark with water, and shake in a rotating machine making 30-40 revolutions per minute for 30 minutes at room temperature. Filter the liquid immediately.

In the case of a double superphosphate, use the same quantity, fill the flask almost to the mark, and let stand 24 hours, shaking at frequent opportune moments. Then fill to the mark, shake, and filter. Determine the phosphoric acid in the filtrate by the citrate method, as directed under 5.

In the case of superphosphates and double superphosphates containing more than 20 per cent of phosphoric acid, take 25 cc. of the solution, equivalent to 0.5 gram of material, but use the same quantities of reagents. To convert the pyrophosphoric acid in double superphosphates into precipitable orthophosphoric acid, boil 25 cc. of the solution 10 minutes with 10 cc. of nitric acid, sp. gr. 1.40. After the addition of the ammoniacal citrate solution add a quantity of ammonia equivalent to the nitric acid and then proceed as with the ordinary superphosphates.

CITRATE-SOLUBLE PHOSPHORIC ACID

The citrate-soluble phosphoric acid of superphosphates and superphosphate mixtures should be determined according to Petermann's method, p. 200, and must be stated, upon demand. The sum of the water-soluble and citrate-soluble phosphoric acids must not be termed citrate-soluble.

¹ *Chem. Ztg.*, **8**, 1743 (1884).

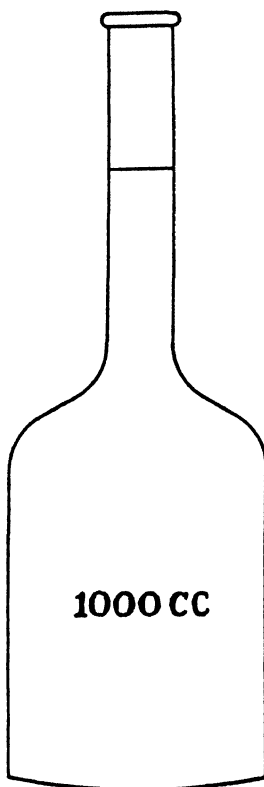


Fig 12.—Stohmann Flask.

7 REAGENT

Petermann's ammonium citrate solution.—The following directions for the preparation of ammonium citrate solution are more easily and accurately carried out than the original direction of Petermann.¹

For each liter of the solution to be made, dissolve 173 grams of pure, non-defloresced, crystallized citric acid and add, slowly and with cooling, sufficient aqueous ammonia, the concentration of which has been ascertained by titration, to give 42.0 grams of ammoniacal nitrogen per liter of the final solution. The ammonia required is 563.9 cc. (sp. gr. 0.960 $\frac{15^{\circ}}{15^{\circ}}$) since this contains 78.22 grams of ammoniacal nitrogen per liter. Cool to 15° C. and fill to the required volume with water of 15° C. temperature. The specific gravity of the solution is 1.082 to 1.083 $\frac{15^{\circ}}{15^{\circ}}$.

¹ Landw. Vers. St., 60, 241 (1904).

Determine the nitrogen content as well as the specific gravity as a control of the final solution. Dilute 25 cc. to 250 cc. and take 25 cc., equivalent to 2.5 cc. of the original solution. This must contain 0.1050 gram of nitrogen.

8 DETERMINATION

Proceed as directed under 8, p. 200, but determine phosphoric acid (P_2O_5) in the citrate-soluble extract only.

CITRIC ACID-SOLUBLE PHOSPHORIC ACID

9 PREPARATION OF SOLUTION

Place 5 grams of Thomas phosphate meal in a dry 500 cc. Stohmann flask, the neck of which should have at least a 2 cm. internal diameter and extend at least 8 cm. beyond the mark. Pour 2 per cent citric acid at 17.5° C. upon the sample, fill to the mark, and shake exactly 30 minutes in a rotating apparatus making 30-40 revolutions per minute. Filter immediately at the expiration of this time. Although the Lorenz molybdate method has proved reliable, determine the phosphoric acid (P_2O_5) in the filtrate, for the present, by the ferric citrate method as described under 11. If difficulties are encountered in this method, use the hydrochloric acid method with separation of silicic acid, as directed under 12.

By 2 per cent citric acid is meant an aqueous solution containing 2 parts by weight of crystallized citric acid per 100 parts by volume of the solution.

First prepare a stock solution of five times the strength, *i. e.*, a 10 per cent solution in the sense mentioned, by dissolving 1 kg. of chemically pure, crystallized, non-defloresced citric acid in water and diluting this solution to 10 liters. (The solution can be preserved by the addition of 5 grams of salicylic acid.) Test for the acid concentration of this stock solution.

Dilute 50 cc. of the stock solution to 500 cc. and take 50 cc., corresponding to 0.5 gram of citric acid. Titrate this with the standard alkali used in nitrogen determination, using phenolphthalein as indicator. (Since citric acid, $C_6H_8O_7 + H_2O$, has the molecular weight 210.11 and neutralizes 42.03 nitrogen, and both figures are almost exactly in the ratio 5:1, the quantity of crystallized citric acid contained in 1 liter of the stock solution is the same numerically as the quantity of nitrogen, expressed in milligrams, equivalent to the standard alkali solution used for the neutralization.)

Example: 1 cc. of standard alkali solution is equivalent to 2.532 mg. of nitrogen. For neutralization of 50 cc. of the citric acid, diluted as stated, 39.5 cc. was used. One liter of the stock solution therefore contains $2.532 \times 39.5 = 100.0$ grams of crystallized citric acid, which is as it should be.

Dilute 1 part by volume of the stock solution with water to 5 parts by volume and thus obtain the 2 per cent citric acid.

10 REAGENTS

(a) *Ferric citrate solution.*—Place 1.25 liters of citric acid solution containing 800 grams per liter in a glass bottle provided with a mark at the 5 liter level. (This bottle should not be too sensitive to temperature changes.) Dissolve 30 grams of ferric chloride (undecomposed, easily soluble to a clear solution) in about 50 cc.

of water, warm slightly, pour the solution into the citric acid, and rinse with a little water. Add very slowly and with vigorous stirring and cooling, 3.5 liters of ammonia (sp. gr. 0.91 $\frac{15^\circ}{15^\circ}$).

The ferric citrate solution contains in one-half the volume the same quantities of citric acid and ammonia as the ammonium citrate solution described under 4 (a). To test, proceed exactly as stated there except to use 25 cc. per liter, instead of 50 cc., of the diluted solution, which is equivalent to 0.625 cc. of the original ferric citrate solution. With all loss of ammonia avoided, these solutions should contain the same quantities of ammonia as stated under 4 (a).

(b) *Hydrogen peroxide*.—Dilute 100 cc. of 30 per cent Perhydrol Merck to 1 liter. (The preservation of the solution is improved by the addition of 5 cc. of alcohol.) A solution of equal effectiveness can be made from sodium perborate. Dissolve about 150 grams of sodium perborate and 60 grams of citric acid in sufficient water to make 1 liter, but first find the correct quantity of sodium perborate by titration of a test solution. To aid in the preservation of the solution, add 5 cc. of alcohol (50 cc. of the solution, ready for use, when evaporated to about 10 cc., must not show any cloudiness, even on prolonged standing, after the addition of some ammonium chloride, ammonia and magnesia mixture). Determine the content iodometrically or by means of titanous chloride.

11 DETERMINATION

(Ferric Citrate Method)

To 50 cc. of the solution, prepared as described under 9, and equivalent to 0.5 gram of material, add 25 cc. of ferric citrate solution, 1 cc. of 3 per cent hydrogen peroxide, and 25 cc. of magnesia mixture in the order named and stir or shake 30 minutes. The precipitate may be filtered immediately or after standing several hours. Complete the determination as directed under 5.

12 DETERMINATION

(Hydrochloric Acid Method)

Evaporate almost to dryness on the water bath 100 cc. of the citric acid extract, under 9, with the addition of about 5 cc. of 25 per cent hydrochloric acid. Take up the residue with about 2 cc. of 25 per cent hydrochloric acid, disintegrate the silicic acid by rubbing with a rubber wiper, and wash into a 100 cc. flask. Then bring the liquid to a boil, cool, fill to the mark, and filter. Use 50 cc. of the filtrate, equivalent to 0.5 gram of material, for the phosphoric acid determination and proceed as directed under 5.

13 MECHANICAL ANALYSIS OF THOMAS PHOSPHATE MEAL

Place 50 grams of Thomas phosphate meal on a sieve with a surface of not less than 20 cm. diameter and made from wire mesh No. 100, made by Amandus Kahl, Hamburg (smooth mesh). Shake the sample 15 minutes by hand or in a shaking machine and weigh the coarse meal remaining on the sieve.

*Verein Deutscher Dünger Fabrikanten*¹**TOTAL PHOSPHORIC ACID****I PREPARATION OF SOLUTION**

(a) *Rock phosphates*.—Pour 50 cc. of aqua regia over 5 grams of the finely ground material in a 500 cc. flask and evaporate approximately to the consistency of a sirup in order to render the silicic acid insoluble. Take up the residue, which after cooling should have almost solidified but not have become dry, with 10 cc. of nitric acid (sp. gr. 1.2) and 50 cc. of water. After cooling fill to 500 cc. and filter. Determine the phosphoric acid in the filtrate by the molybdate-magnesium method only, as directed under 3.

(b) *Superphosphates*.—Boil 10 grams of superphosphate 30 minutes with about 100 cc. of water and 50 cc. of sulfuric acid (sp. gr. 1.4). Cool, and fill to 500 cc. Determine phosphoric acid in the filtrate by the citrate method as directed under 5.

(c) *Guanos, bone meals and fish meals*.—Dissolve the material as in the procedure prescribed under the analysis of rock phosphates. Determine the phosphoric acid in the filtrate by the citrate method, as directed under 5 (Ignition and ashing of the sample before solution is not recommended since it causes losses in most cases.)

(d) *Precipitated phosphates*.—Dissolve according to the directions under rock phosphates. Determine the phosphoric acid by the citrate method as directed under 5.

(e) *Thomas phosphate meals*.—Sieve Thomas slag meals that contain coarse particles through a 2 mm. sieve and crush the coarser particles on the sieve by the application of slight pressure. If there is still a residue, weigh it and exclude it from the analysis and consider it as a worthless constituent.

Add a few cc. of dilute sulfuric acid (1 + 2) to 10 grams of phosphate meal and shake well. After adding 50 cc. of concentrated sulfuric acid warm the mixture until thoroughly decomposed, add water before thoroughly cooled, shake as much as necessary to disintegrate any crusts present or boil again, cool, and dilute to 500 cc., disregarding any undissolved material. Do not delay too long in filling to the mark and mixing as there may then be difficulty in distributing uniformly the concentrated solution that becomes enveloped by the undissolved matter. Determine phosphoric acid in 50 cc. of the filtered solution (corresponding to 1 gram) according to the citrate method, under 5, using, however, 100 cc. of ammonium citrate solution instead of 50 cc. Since the precipitate is less easily separated out completely than in the case of superphosphates, stir vigorously and take special care that the ammonia content of the citrate solution is not too small.

(f) *Ignited phosphates*.—Carry out the determination of total phosphoric acid as in rock phosphates.

2 REAGENTS

(a) *Aqua regia*.—Mix 3 parts of hydrochloric acid (sp. gr. 1.12) and 1 part of nitric acid (sp. gr. 1.2).

¹ Methoden zur Untersuchung der Kunstdüngemittel. 6th ed. Verein Deutscher Dünger-Fabrikanten. Braunschweig, 1925.

(b) *Molybdate solution*.—Gradually introduce 150 grams of finely powdered ammonium molybdate into approximately 400 cc. of hot water. After cooling dilute to 1 liter and slowly add with shaking 1 liter of nitric acid (sp. gr. 1.2). Let stand 24 hours, filter, and preserve in the dark.

(c) *Magnesia mixture*.—Dissolve 55 grams of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and 70 grams of ammonium chloride in water, add 250 cc. of ammonia (sp. gr. 0.96), and dilute to 1 liter.

(d) *Wash water for the molybdate precipitates*.—Bring 32 cc. of nitric acid (sp. gr. 1.2) and 50 grams of ammonium nitrate to 1 liter by solution in water.

(e) *25 per cent ammonia*.—Dilute 100 cc. of 25 per cent ammonia (sp. gr. 0.91) to 1 liter with water.

3 DETERMINATION

(Molybdate-Magnesium Method)

Precipitation of the yellow molybdate precipitate.—Add an abundance of molybdate solution (at least 100 cc. for each 0.1 gram of P_2O_5) to 50 cc. of the filtered solution prepared as directed under 1 (a) and digest an hour at 50°C . on a water bath. Allow to stand a sufficiently long time and filter through a small, dense filter paper. Test the filtrate by the addition of more molybdate solution, warming to 50°C ., and allowing it to stand for 12 hours to see that precipitation is complete. Wash the precipitate by repeated decantation with the wash water, 2 (d), until a reaction for lime is no longer given. Make the test for lime by adding a little sulfuric acid and 2 cc. of alcohol to 1 cc. of the wash water; the presence of lime is shown by a precipitate or cloudiness. Five decantations with 20 cc. of wash liquid are usually sufficient.

Solution of the yellow precipitate.—Dissolve the residue in the beaker with 80-100 cc. of 2.5 per cent ammonia and pour through the filter. Dissolve any precipitate remaining in the filter by washing with ammonia. Finally wash the beaker and filter with hot water.

Precipitation with magnesia mixture.—Heat the solution of the yellow precipitate, which should not exceed a volume of 150 cc., until bubbles just begin to pass off, and precipitate immediately by adding 20 cc. of magnesia mixture dropwise with constant stirring. Let stand at least 4 hours, filter, and wash with 2.5 per cent ammonia until a reaction for chlorine is no longer shown. Gooch or Neubauer crucibles are preferable to filter papers.

Ignition and weighing.—Dry the filter and precipitate, place in a weighed platinum crucible, ash carefully in such a manner that the filter chars without giving a flame, then ignite several minutes over a burner giving an intensive flame, but not over a blast. (An electric furnace at 1100°C . is most satisfactory.) After cooling, weigh. Repeat the ignition until constant weight is reached. Make sure that the ignited precipitate is entirely white by crushing it.

Factors for the calculation:

$$\text{Mg}_2\text{P}_2\text{O}_7 \times 0.6379 = \text{P}_2\text{O}_5; \quad \text{P}_2\text{O}_5 \times 2.184 = \text{Ca}_3(\text{PO}_4)_2$$

4 REAGENTS

(a) *Ammonium citrate solution*.—Add a little water to 100 grams of pure citric acid and dissolve slowly and with cooling by the addition of 350 cc. of 25 per cent

ammonia liquor (sp. gr. 0.91). Cool, and bring to 1 liter with water and filter before use.

(b) *Magnesia mixture*.—Prepare as directed under 2 (c).

5 DETERMINATION

(Citrate Method)

To 50 cc. of the solution prepared as directed under 1 (b), 1 (c), 1 (d) or 1 (e) (or 25 cc. if it contains more than 20 per cent P_2O_5) add 50 cc. of the ammonium citrate solution and 25 cc. of magnesia mixture. Stir for 30 minutes in the beaker, and filter after settling. Add the 25 cc. of magnesia mixture rapidly and with stirring. Filter, wash, ignite, and weigh the precipitate as directed under 3 for the molybdate-magnesium method.

6 WATER-SOLUBLE PHOSPHORIC ACID

(a) *Superphosphates*.—Make an aqueous extract by placing 20 grams of superphosphate in a liter flask, adding 800 cc. of water, and shaking continuously and strongly for 30 minutes; then bring to the mark with water, shake the whole liquid well, and filter. (Machines that are driven by hand or motor may be used for shaking, and 150 alternations per minute for shaking machines or 30-40 revolutions per minute for rotational machines are recommended. The flask may be filled to the mark immediately when a rotational machine is used.) Determine the phosphoric acid by the citrate method as directed under 5. In the case of double superphosphates make the following modifications:

Prepare the extract by allowing 20 grams to stand in contact with about 800 cc. of water in a liter flask for 24 hours, shaking frequently during this period, filling to the mark, and filtering. Boil 25 cc. of this filtrate with 10 cc. of concentrated nitric acid (sp. gr. 1.4) for 10 minutes to convert any pyrophosphoric acid present into orthophosphoric acid. After the addition of the ammonium citrate solution, add a quantity of ammonia liquor equivalent to the addition of the nitric acid.

(b) *Guanos, bone meals and fish meals*.—Determine the water-soluble phosphoric acid according to the directions given in (a) for the determination of water-soluble phosphoric acid in superphosphates.

CITRATE-SOLUBLE PHOSPHORIC ACID¹

7 REAGENTS

Petermann's ammonium citrate solution, original directions.—Dissolve 500 grams of citric acid in ammonia (sp. gr. 0.91) to neutral reaction, for which about 700 cc. ammonia is necessary (indicator: rosolic acid). Cool, and bring to the specific gravity of 1.09 at 15° C., then add 50 cc. of ammonia (sp. gr. 0.91) per liter and, after allowing to stand 48 hours, filter. (The specific gravity of the final solution is 1.082-1.083.)

Directions of the Verband landwirtschaftlicher Versuchsstationen.—See par. 7, p. 194.

¹ This procedure gives the available, water-soluble plus citrate-soluble, phosphoric acid. (Authors).

8 DETERMINATION

(a) *Superphosphates*.—Grind 2.5 grams of the dry superphosphate or ammonium superphosphate in a small mortar, then grind further after the addition of 20-25 cc. of water. Decant the liquid upon a filter paper and filter into a 250 cc. flask. Treat the residue in the mortar three more times in the same manner. Take special care when grinding with the water to grind vigorously and continuously until the material becomes a fine powder, which no longer grates. Place the residue upon the filter and wash with water until the filtrate is about 200 cc. If the filtrate is cloudy, add a few drops of nitric or hydrochloric acid and fill to 250 cc. Place the filter with the residue in a 250 cc. flask with a wide neck and shake with 100 cc. of Petermann's ammonium citrate solution until the filter has been completely disintegrated. Stopper the flask while so doing and keep closed until the digestion is complete. Allow the Petermann solution to act either 15 hours at room temperature and then an hour on the water-bath at 40° C., or 4 hours at 40° C. Shake the flask about every 15 minutes during the digestion on the water-bath. After cooling, fill to the mark with water and filter. For the analysis mix 50 cc. of the aqueous solution with 50 cc. of the solution obtained by the action of Petermann's solution and then proceed by the molybdate-magnesium method or by the citrate method. Precipitation by the citrate method is done as proposed by Neubauer by the addition of 25 cc. of a solution containing 55 grams of crystallized magnesium chloride, 70 grams of crystallized ammonium chloride, 61.6 grams of crystallized citric acid, and 625 cc. of ammonia (sp. gr. 0.91). Allow the precipitate to stand after stirring, preferably overnight.

(b) *Precipitated phosphates*.—The valuation of precipitated phosphates is based mostly on their citrate-soluble phosphoric acid content. Grind 1 gram of precipitated phosphate with Petermann's citrate solution in a mortar, and wash into a 250 cc. flask. Do not use more than 100 cc. of the citrate solution for grinding and transferring. Allow to stand 15 hours at ordinary temperature with shaking, then digest 1 hour at 40° C. on the water-bath, fill to the mark with water after cooling, and filter. Boil 50 cc. of the filtrate 10 minutes with 10 cc. of concentrated nitric acid. Precipitate the phosphoric acid by the molybdate-magnesium method or by the citrate method. In the citrate method neutralize approximately with ammonia, add 15 cc. of Petermann's solution and 10 cc. of ammonia (sp. gr. 0.91), and precipitate with 25 cc. of magnesia mixture, as in the citrate method described under 5. (A rotation for 3 hours has proved in most cases equivalent to the 15 hours' digestion. With many precipitated phosphates of dense character, even this is not sufficient to dissolve all the dicalcium phosphate. In such a case a 7 hour digestion on the water-bath at 40° C. without preliminary rotation may alone be considered reliable.)

(c) *Rhenania phosphates*.—Place 2.5 grams of Rhenania phosphate in a dry Stohmann flask and add 250 cc. of Petermann's solution, then either (1) shake an hour with 30-40 turns per minute in a rotational shaking machine, or (2) place in a water-bath at 40° C. for 4 hours, shaking once every half hour. Then cool to room temperature. Pour the solution from (1) or (2), without previously diluting, through a dry filter into a dry vessel. Boil 50 cc. of the filtrate, corresponding to 0.5 gram of material, for a few minutes with 50 cc. of water and 20 cc. of con-

centrated sulfuric acid. Determine the phosphoric acid by one of the usual procedures, best by the Lorenz molybdate method; (1) and (2) give results which agree.

CITRIC ACID-SOLUBLE PHOSPHORIC ACID

9 PREPARATION OF SOLUTION

Thomas phosphate meals and ignited phosphates.—Place 5 grams in a dry Stohmann half-liter flask, the neck of which should be at least 2 cm. internal diameter and the length at least 8 cm. beyond the mark, add 2 per cent citric acid (17.5° B \acute{e} .) to the sample, filling to the mark, and rotate exactly 30 minutes in a rotational machine that makes 30-40 turns a minute. Filter immediately through a dry filter into a dry vessel. In the case of Thomas phosphate meals determine the phosphoric acid in the filtrate by the ferric citrate method but use the hydrochloric acid method in referee cases. In the case of ignited phosphates determine the citric acid-soluble phosphoric acid by the Lorenz¹ molybdate method, under 14, as carried out by Neubauer-Lucker, since the ferric citrate method may fail, owing to the high silica content.

10 REAGENTS

(a) *Ferric citrate solution.*—Prepare as described under 10 (a), p. 195.

(b) *Hydrogen peroxide solution, 3 per cent.*—Prepare as described under 10 (b), p. 196.

(c) *Magnesia solution*—Prepare as described under 2 (c).

11 DETERMINATION

(Ferric Citrate Method)

Proceed as directed under 11, p. 196.

12 DETERMINATION

(Hydrochloric Acid Method)

Proceed as directed under 12, p. 196.

13 REAGENTS

Prepare as directed under 2 (a) to 2 (c), pp. 191-2.

14 DETERMINATION

(Lorenz Molybdate Method)

The phosphate solution should amount to 50 cc., and contain 0.08-1.5 cc. of free concentrated sulfuric acid (sp. gr. 1.84); 10-20 grams of free nitric acid, corresponding approximately to 25-50 cc. of nitric acid (sp. gr. 1.40); not more than 0.050 gram P₂O₅; not more than 0.5 gram of hydrochloric acid; 1 gram of citric acid; 1 gram of ammonium salts; 0.5 gram each of sodium salts, potassium chloride, iron oxide, alumina, magnesia, manganese salts and calcium salts; 5 grams of potassium nitrate; and 1 gram of potassium sulfate. Larger quantities of sulfates cause the results to be too low.

¹ *Landw. Vers.-Sta.*, **55**, 183 (1901); **89**, 342 (1917); *Z. anal. Chem.*, **51**, 161 (1912).

Fertilizer solutions prepared in the usual manner and of which only 10-20 cc. is used always contain less than the maximum quantities given above and hence offer no difficulties.

Measure out into a beaker holding about 250 cc., 10-20 cc.—according to the P_2O_5 content—of the solution prepared in the customary manner. To get accurate delivery, carefully calibrate and provide the pipet with arms of small diameter and a fine tip. Bring the volume to 50 cc. with the sulfuric acid-nitric acid mixture in case the phosphate was not dissolved with sulfuric acid, or with the diluted nitric acid (sp. gr. 1.19-1.21) if it was dissolved with sulfuric acid. Heat over a wire screen under a hood, without using a glass rod, until bubbles due to initial boiling appear; remove from the flame; shake with a rotary movement for a few seconds so that the walls of the vessel are no longer overheated; pour immediately, from an approximately accurate measuring cylinder, 50 cc. of sulfate-molybdate reagent into the middle of the solution; and allow to stand covered. (If conditions permit a smaller volume, 25-30 cc. may be used and precipitated by an equal volume of the molybdate reagent, involving a saving of the latter. In order to obtain accurate results it is only essential that the composition of the solution before precipitation correspond to the conditions prescribed when referred to a 50 cc. basis and that an equal volume of the molybdate reagent be used.) As soon as most of the precipitate has settled, but at most after 5 minutes, stir vigorously with a glass rod for 30 seconds. When large numbers of analyses are to be carried out, glass vessels that are somewhat smaller toward the top are perhaps more suitable in order more certainly to prevent the danger of spattering of the phosphoric acid solution by the nitric acid vapors upon boiling. On removing these vessels from the flame, shake with a rotary motion about 10 seconds in order to equalize any overheating, pour in the 50 cc. of sulfate-molybdate reagent rapidly and without touching the glass walls, let stand at most 5 minutes, and then shake vigorously with a rotary movement the prescribed 30 seconds instead of stirring with a rod. After 5-18 hours (if less than 3 mg. of P_2O_5 is expected, after 12-16 hours) filter through a Gooch crucible with the help of a suction pump.

Detailed instructions in regard to the crucible to be used and its handling are as follows:

After the liquid over the precipitate has run through, wash without delay at least 5 times with the 2 per cent ammonium nitrate solution, taking care that particles of the yellow precipitate that adhere to the glass are brought into the crucible by means of a rubber-tipped stirring rod. Immediately fill the crucible once and then half fill it twice with acetone, sucking it off each time. Carefully wipe off the crucible externally and place it at once in a space with the highest vacuum possible, having in any event not more than a 150 mm. air pressure (see below for more detailed instructions). After allowing to remain at least 30 minutes in this space, weigh the crucible immediately or place, until weighed, in a desiccator containing a mixture of equal volumes of water and concentrated sulfuric acid. Multiply the weight of the ammonium phosphomolybdate, which contains 3.295 per cent of P_2O_5 , by 0.03295 to obtain the phosphoric acid present.

Check on the accuracy of the analyses.—The two salts, monopotassium phosphate (KH_2PO_4) and monoammonium phosphate ($NH_4H_2PO_4$), are well suited as materials for a test of the accuracy of the results which is especially desirable in

the case of the Lorenz molybdate method. Monopotassium phosphate contains 52.175 per cent of P_2O_5 ; and monoammonium phosphate, 61.722 per cent of P_2O_5 . Dry the salts in weighing glasses at about 100° C. and then weigh out 6.3153 grams of KH_2PO_4 , or 5.3385 grams of $NH_4H_2PO_4$. Dissolve the weighed salt in a standardized flask and bring to 200 cc. Preserve the stock solutions in these flasks with close-fitting stoppers. Dilute 20 cc. to 200 cc. Then 20 cc. of this diluted solution contains 0.03295 gram of P_2O_5 , and should give by this method 1.0000 gram of precipitate. In order to proceed with certainty in this check, before making up the diluted solution the analyst may add the other constituents present in the solution that is being analyzed, *e. g.*, a corresponding quantity of citric acid in the case of the determination of citric acid-soluble phosphoric acid.

The crucible and its treatment.—Lorenz recommends platinum Gooch crucibles with paper filters, and gives the following directions:

The crucible is not provided with asbestos, but a circular disk of smooth, air-dry, not too dense, but ash-free and fat-free filter paper is placed upon the smooth bottom of the crucible; it is cut so that it does not touch the walls of the crucible but sufficiently covers the openings in the bottom. The crucible, of which the weight with the filter paper disk is known, is placed in the usual manner in the filtering apparatus, which is connected with a water pump and provided with a lateral stop-cock, the disk is sucked dry by means of the pump, some water is poured on it and the molybdate precipitate is filtered through the crucible. The filter paper disk for the Gooch crucible is cut from Schleicher and Schull fat-free paper (No. 571) that is used for milk analyses and washed with nitric acid since it contains 0.6 per cent ash when unwashed; this ash content, however, is not of much importance since the disk weighs only 30-70 mg. It is possible that other ash-free and fat-free papers may be just as or even more suitable. The correct degree of air-dryness of the filter paper disk is obtained by drying first for about 1 hour at about 105° C. and then letting it lie exposed to the air about 24 hours. It then contains about 5 per cent of hygroscopic water and changes its weight from day to day with the prevailing humidity of the atmosphere, but only by a few tenths of a per cent, *i. e.*, only a few tenths of a milligram, if the weight of the filter is less than 0.1 gram. The filter paper disks may be cut by the thousand to furnish a supply, and, after they have been given the preliminary treatment, may be weighed by the thousand, the weight being recorded on each disk with a lead pencil (the graphite streaks do not cause any perceptible change of weight). The Gooch crucible will last through hundreds of determinations without changing its lustrous appearance and is therefore given a constant weight, and the weight of each filter disk is added for each analysis.

Crucibles with a platinum sponge filter (Neubauer crucibles) are much more convenient. The weight of the empty crucible is the same whether it has been dried after treatment with acetone in the partially exhausted space, by warming, or by igniting. Previous to each filtration the dry precipitate is brushed out with a medium soft brush, and the last traces are removed by sucking a little dilute ammonia through the crucible and displacing this with water. The crucibles customarily do not change weight even after a week's use, and it is therefore sufficient to check the tare again only after about 10 filtrations. The rapidity of filtration, which decreases somewhat with time, can in most cases be restored by merely

igniting gently. If this treatment does not suffice, it is advisable to fuse an easily fusible mixture of potassium and sodium carbonates in the crucible until it penetrates through the holes in the bottom, then boil the crucible with water, wash, and finally treat with some nitric acid. This operation and the ignition which is necessary from time to time must be carried out with extraordinary care so that the layer of sponge does not develop the slightest crevice, as otherwise cloudy filtrates are obtained immediately. If, however, a crack does appear in the layer of platinum sponge, the crack should be smeared with a little platinum black, contact with the rest of the filtering surface being avoided, and the crucible should then be ignited. Since the crucibles need only be ignited gently and occasionally, those of a platinum-gold alloy containing about 90 per cent gold and 10 per cent platinum, which are decidedly cheaper, may be used in place of the platinum crucibles.

Vacuum evaporation of the acetone.—Lorenz used a single pump for both filtration and evacuation, but it is more practicable to use a separate pump for the drying equipment. Since the precipitate only gives up with difficulty any moisture it has attracted from the air, it is advisable to place each precipitate which has been sucked dry immediately in the drying chamber, even though a short period of exposure to the air causes no appreciable error. Several crucibles, however, can be placed in the same vacuum chamber, but the vacuum must be again increased upon the introduction of each crucible. For continuous work on a large scale it is much more convenient and reliable to use a special vacuum apparatus,¹ as proposed by Soxhlet, which is so arranged that each crucible can be placed singly under a small glass cap which is linked with the pump and a common manometer as well as with the outer air. Drying should be at the highest vacuum obtainable. The precipitates on weighing must not smell of acetone. In cases of doubt drying should be continued.

Separate collection of the acetone.—To recover the acetone easily it must be collected separately in the filtration. Two filtering flasks, one of white glass for the aqueous filtrate and the other of brown glass for receiving the acetone, are used. The filter tube into which the crucible is placed with the usual rubber tubing is provided below with a ground edge which passes into the openings of both filtering flasks. This ground edge allows the glass tube with the crucible to be removed much more easily and quickly after admission of air and placed upon the other flask than if it were provided with a rubber stopper. Both filtering flasks are attached to the suction pump with rubber tubing through a three-way stopcock which permits connection of each flask with the pump and the outer air. The double suction flasks mentioned by Mach² may also be used advantageously for separate collection of the acetone.

FREE PHOSPHORIC ACID

The following methods are used for the determination of free phosphoric acid in superphosphates:

¹ The firm of C. Gerhardt, Bonn, furnishes this equipment made entirely of glass, without any rubber or metal connections, for 8 crucibles.

² *Chem. Ztg.*, **37**, 651 (1913). These flasks may be obtained in various sizes from Wagner and Muntz, München, Karlstr. 43.

15 DETERMINATION

(a) *Titration method.*—Dilute 50 cc. of the water-soluble phosphoric acid solution of the superphosphate, prepared as directed under 6 (a) with water to about 300 cc. and add 3 drops of methyl orange, or methyl orange indigo, as indicator. Titrate with 0.5 *N* sodium hydroxide solution, 1 cc. of which corresponds to 0.0355 gram of P_2O_5 .

Prepare the methyl orange by diluting 20 cc. of a solution containing 1 gram of the indicator per liter and the methyl orange indigo by diluting to the same volume 60 cc. of a solution containing 1 gram of sodium indigo sulfate per liter.

(b) *Alcohol method.*—Place 5 grams of the superphosphate in a 250 cc. flask, fill to the mark with absolute alcohol, shake 30 minutes, and filter. Evaporate 50 cc., corresponding to 1 gram, to dryness on a water bath; take up the residue with hot water, filter into an Erlenmeyer flask, washing the residue on the filter; and titrate with 0.5 *N* sodium hydroxide, using 3 drops of methyl orange as indicator.

16 MECHANICAL ANALYSIS OF THOMAS PHOSPHATE MEALS

Proceed as directed under 13, p. 196.

FRANCE¹

Commercial phosphatic materials are divided into five classes, as follows:

1. *Mineral phosphates*, composed of tricalcium phosphate, more or less mixed with calcium carbonate, silicious matters, iron and aluminum oxides, etc.
2. *Ground raw bone phosphate*: degelatinized bone phosphate; bone black; spent sugar-refinery black; etc.
3. *Phosphates* in such products as manure, dried powdered night soil, guano, etc.
4. *Chemically treated phosphates*: bone or mineral superphosphates; precipitated phosphates; ammonium magnesium phosphate.
5. *Phosphatic slags* produced in metallurgical processes.

TOTAL PHOSPHORIC ACID

I PREPARATION OF SOLUTION

(a) *Class 1 materials.*—Introduce 2 grams of the phosphate into a flask with 10-15 cc. of hydrochloric acid and bring to boiling for 5 minutes, avoiding any desiccation. Then add 2 or 3 cc. of hydrochloric acid and dilute the solution with water, bringing the volume to exactly 200 cc. Mix; filter; take 100 cc., representing 1 gram of material; and proceed for the determination of phosphoric acid by the citrate method as described under 3, or by the molybdate-magnesium method as

¹ Méthodes d'Analyse des Engrais. Ministère de l'Agriculture. Paris. 1897.

described under 5. The citrate method, which is recommended, is based on the precipitation of phosphoric acid as magnesium ammonium phosphate in ammoniacal solution, and on the property of ammonium citrate of keeping in solution the calcium, aluminum and iron which always accompany the phosphoric acid.

(b) *Class 2 materials*.—Calcine materials of the second class before the addition of the hydrochloric acid and then proceed as for class 1 materials.

(c) *Class 3 materials*.—Mix 4 grams of the material in a porcelain crucible with 0.2 gram of slaked lime, in order to prevent possible reduction of the phosphoric acid by the organic matter, which would cause loss of phosphorus. Moisten the mixture with 10 drops of water, dry on a sand bath, and carefully ignite in a muffle, bringing to a red heat only after liberation of gas has entirely ceased. Remove the ignited mass and place in a flask; wash the crucible with hydrochloric acid and then with water into the flask. Boil for some minutes, cool, and dilute to 200 cc. Filter; take 100 cc., corresponding to 2 grams of material; and proceed as for class 1 materials.

(d) *Class 4 materials*.—Proceed in the case of precipitated phosphates as for materials of the first class, but take an aliquot corresponding to only a 0.5 gram sample because of the high phosphoric acid content.

(e) *Class 5 materials*.—In the case of phosphate slags, treat 2 grams in a beaker with 15 cc. of hydrochloric acid; heat for 10 minutes on a sand bath, add 10 cc. of nitric acid to oxidize the iron, and evaporate to dryness on the sand bath. This evaporation should be made with extreme care; if not carried far enough the silica will not be rendered insoluble, which would make filtration extremely slow, and would give too high results. To assure complete desiccation, not only must no odor of acid be perceptible but the mass should assume an ochreous color. Add 10 cc. of hydrochloric acid, heat several minutes on the sand bath, add hot water, continue heating several more minutes, cool, bring to exactly 200 cc., filter, take 100 cc., corresponding to 1 gram of material, and proceed as for class 1 materials.

The preliminary attack with hydrochloric acid is necessary because nitric acid cannot dissolve the phosphates entirely. When the slags are very rich in lime, as is frequently the case, it can be eliminated by means of ammonium oxalate in acetic acid solution.

(f) *Phosphatic materials in general*.—In spite of all precautions, the precipitation of magnesium ammonium phosphate by the citrate method almost always entrains a little silica, and iron and aluminum oxides, as well as lime. This can be partly overcome by attacking the material with sulfuric acid, which has the advantage of dissolving less silica as well as lime. The procedure is as follows:

Treat 5 grams of phosphate in a 500 cc. flask with 20 cc. of nitric acid (sp. gr. 1.4) and 50 cc. of pure sulfuric acid. Boil for 30 minutes; cool, bring the volume to 500 cc., mix, and filter. Take 50 cc. of the filtered liquid, representing 0.5 gram of phosphate, and proceed as described under 3.

In the case of phosphate fertilizers containing organic matter, such as guanos, bone phosphates, etc., continue the boiling for 1 hour in order to destroy the organic matter, thus dispensing with the preliminary incineration.

2 REAGENTS

(a) *Ammonium citrate solution*.—Dissolve 400 grams of crystallized citric acid without heating in a sufficient quantity of 22° Bé. ammonia. Dilute to 1 liter with ammonia.

(b) *Magnesia mixture*.—Dissolve 150 grams of crystallized magnesium chloride and 150 grams of ammonium chloride in a sufficient quantity of water to make the volume 1 liter; 10 cc. of this solution precipitates 0.5 gram of phosphoric acid.

(c) *Joulie's citro-magnesia solution*.—Dissolve 22 grams of pure magnesium carbonate in a solution of 400 grams of citric acid in 200 cc. of water, and add about 400 cc. of 21°-22° Bé. ammonia. This solution should remain strongly acid.

3 DETERMINATION

(Citrate Method)

To a 100 cc. aliquot of solution, prepared as directed above, add 40 cc. of ammonium citrate solution, 50 cc. of ammonia, and 10 cc. of magnesia mixture; stir vigorously with a glass rod, avoiding contact with the walls of the beaker in order to prevent the formation of an adherent deposit on the glass, cover the beaker with a watch-glass or place under a bell jar, and allow to stand.

The phosphoric acid is entirely precipitated at the expiration of 2 hours as magnesium ammonium phosphate; if it is desired to hasten the precipitation, stir continuously for about 30 minutes by hand or, better, resort to a mechanical agitator; the precipitation can then be considered as complete at the end of about 1 hour.

Filter the precipitate upon a small filter paper, preferably the plaited kind; detach that adhering to the beaker by means of a policeman and wash onto the filter by means of water containing one-third of its volume of ammonia. Use this mixture also for washing the precipitate on the filter, which can be done with about 50 cc. of the ammoniacal water when care is taken to bring the precipitate into suspension by means of the jet from the wash bottle. Washing is thus much more complete and the plaited filter is of advantage for this purpose. The filter may be entirely filled two or three times with the ammoniacal solution. Dry, and ignite the precipitate, taking the following special precautions in order to obtain a colorless precipitate:

Fold up the dried filter paper containing the precipitate and place in a tared crucible, which is set at the edge of the muffle so as to bring about a slow distillation of the organic matter from the paper, using the greatest care to prevent the paper catching fire. When completely charred, bring the crucible to a bright red heat, or still better, to a white heat, until all the carbon has disappeared.

The washing and method of incineration just indicated gives a white or almost white magnesium pyrophosphate when, by the methods in general use, it remains black or a very pronounced gray. In the latter case it is sometimes recommended, in order to render it white, to moisten with nitric acid and calcine anew. This practice should be rejected for it causes losses.

The weight obtained multiplied by 0.639 gives the phosphoric acid in a gram of the material analyzed. To express as tricalcium phosphate, multiply the weight of the phosphoric acid by 2.18.

It happens sometimes that the magnesium ammonium phosphate contains small quantities of magnesia or lime. This gives too high results and the precipitate is

then more or less flocculent. In this case separate the mother liquor by filtration and redissolve the magnesium ammonium phosphate in the same beaker in which it was precipitated. Pour 10 cc. of water containing 5 per cent of nitric acid on the drained filter and wash with this acidified water into the beaker in which the greater portion of the magnesium ammonium phosphate has been retained. Bring the volume to about 50 cc., add 4 or 5 cc. of ammonium citrate and 2 cc. of magnesia mixture, neutralize with ammonia, and finally add 25 cc. of ammonia. Stir, allow to settle, and collect the magnesium ammonium phosphate, which is now freed from its impurities, on a filter.

In order to avoid the precipitation of lime, which interferes with the determination in cases of materials containing very much limestone, increase the quantity of ammonium citrate, adding, for example 60 cc. in place of the 40 cc. and increase the dilution of the solution in which the precipitation is made to about 250 cc. to decrease the liability of entraining lime and even magnesia.

If the flocculent particles are due to silica, which is generally the case when the precipitation of lime has been prevented as just described, dissolve the weighed magnesium pyrophosphate in nitric acid, dilute with 3 or 4 volumes of water, wash with boiling water, collect and calcine the insoluble silica and subtract its weight from that of the pyrophosphate.

It is very important, in order to precipitate all the phosphoric acid, to have an excess of magnesia present, and this excess should be such as to represent about 0.1 gram of magnesia per 100 cc. of the liquid in which the precipitation is made; that is, an excess of 0.2-0.3 gram of magnesia over the quantity necessary for the formation of magnesium ammonium phosphate. As a consequence, varying quantities of magnesia mixture are added, depending on the presumed proportion of phosphoric acid, so as always to have the desired excess. The proportion of magnesia should be increased also with the quantity of ammonium citrate used, and use may be made of Joulié's citro-magnesian solution, which contains proportional quantities of citric acid and magnesia.

The ammonia should be added only after the addition of the magnesia mixture, as there is then less risk of entraining iron and aluminum phosphates in the precipitate.

It may happen, nevertheless, that the magnesium pyrophosphate obtained is not absolutely pure. It may contain some silica, even when there has been a previous evaporation to dryness, and also phosphates of iron and aluminum. The presence of these two substances may be easily ascertained and correction made as follows, if they are present:

Qualitative tests, which take only a few moments, should always be made.

Dissolve the weighed precipitate in nitric acid in the same vessel in which it has been weighed. Weigh any appreciable residue of silica that remains, and subtract from the weight of the pyrophosphate. Dilute the solution to about 100 cc., neutralize with ammonia until blue to litmus paper, and redissolve the precipitate of magnesium ammonium phosphate that is formed with acetic acid in slight excess. If the solution remains clear at the expiration of several hours, the absence of iron and aluminum phosphates is then confirmed. If they are found, collect and weigh, and decrease the weight of the phosphoric acid (P_2O_5) as calculated from the weight of the magnesium pyrophosphate, after its correction for silica, by 0.25

mg. for each milligram of iron and aluminum phosphates obtained. In many cases a little lime is entrained; when very abundant it should be taken into account. In the majority of cases the above corrections are unnecessary. If they are too large, it is advisable to repeat the determination.

4 REAGENT

Ammonium molybdate solution.—Dissolve 100 grams of molybdic acid in 400 grams of ammonia (sp. gr. 0.95); filter and add drop by drop to 1,500 grams of nitric acid (sp. gr. 1.20), stirring constantly. Allow to stand several days in a warm place and decant the clear portion for use.

5 DETERMINATION

(Molybdate-Magnesium Method)

Calcine 5 grams of the material to destroy organic matter, transfer to a flask, add 20 cc. of water and 20 cc. of nitric acid, boil for 15 minutes, cool, and dilute to 100 cc. For phosphates high in phosphoric acid, take 10 cc. of the solution corresponding to 0.5 gram of material; for fertilizers containing 10-20 per cent phosphoric acid, take 20 cc., and for those containing less than 10 per cent take 40 cc. In each case bring the volume to 50 cc. after the addition of 10 cc. of nitric acid and 6-7 grams of ammonium nitrate crystals. Place the liquid in a 300 cc. beaker and add 50 cc. of molybdate solution for each 0.1 gram of phosphoric acid supposed to be in the liquid. Bring the mixture to 90° C. and maintain for 1 hour in a water bath. At the end of this time determine whether an addition of molybdate solution gives a precipitate in a small portion of the clear liquor. If so, add another 50 cc. and continue the heating at 90° C. for another hour, filter, wash with an aqueous solution containing 3 per cent ammonium nitrate and 1 per cent nitric acid, dissolve with several cubic centimeters of ammonia, and wash the filter with water containing 300 grams of ammonia per liter, using a total of 50 cc. Gradually pour into the solution 10 cc. of magnesia mixture while agitating constantly. Allow to stand 12 hours, filter, wash with 3 per cent ammonia, ignite, and weigh as magnesium pyrophosphate.

When very small quantities of phosphoric acid are present, for example, less than 0.05 gram, collect the phosphomolybdate precipitate on a double filter, one of which serves as a tare for the other; wash, with water acidulated with nitric acid and finally with several drops of water, and dry at not exceeding 90° C. The weight multiplied by 0.0376 gives the weight of phosphoric acid.

CITRATE-SOLUBLE PHOSPHORIC ACID

6 DETERMINATION

Precipitated phosphates.—For precipitated phosphates of the fourth class, both total phosphoric acid and that soluble in ammonium citrate are determined. For citrate-soluble phosphoric acid, take 0.75 gram and triturate in a mortar with several drops of citrate solution in order to bring it into a pasty state easily miscible with the solution; gradually mix this paste with 60 cc. of ammonium citrate solution and introduce into a 150 cc. graduated flask, using a part of the citrate solution for washing the mortar. Shake the flask frequently and digest for 12 hours. If there

is a considerable deposit noticeable, again shake and digest for 12 hours more. Dilute to 150 cc., thoroughly mix, filter, and take 100 cc. of the filtered liquid, representing 0.5 gram of material, for the precipitation; proceed as described under 8 for the determination of citrate-soluble phosphoric acid in superphosphates.

WATER-SOLUBLE AND CITRATE-SOLUBLE PHOSPHORIC ACID

7 PREPARATION OF SOLUTION

Superphosphates and chemical fertilizers.—In the case of superphosphates and chemical fertilizers, both water-soluble and citrate-soluble phosphoric acid should be determined. When the fertilizer does not contain magnesium, direct treatment with ammonium citrate dissolves the phosphoric acid existing in both forms, but when magnesium is present, magnesium ammonium phosphate, which is insoluble in the citrate solution, forms and all the phosphoric acid corresponding to the magnesium escapes the citro-ammoniacal treatment. The magnesium exists in the material as sulfate or water-soluble phosphate. It can, therefore, be eliminated by washing, and the treatment with ammonium citrate can be carried out on the residue. The washing with water, however, must be carried out very rapidly so that any free sulfuric acid does not render undissolved phosphate soluble and thus give a greater quantity of soluble phosphoric acid in the results than actually exists in the product under examination.

Pass the material through a 1 mm.-mesh sieve, weigh out 1.5 grams, and place in a glass mortar. Add about 20 cc. of distilled water, stir lightly without crushing, allow to stand a minute, and decant on a non-plaited filter into a 150 cc. graduated flask. Repeat the addition of water and decant 3 or 4 times, working rapidly; then crush the material very finely, collect on the filter by means of a wash bottle, continue the washing to the mark, and mix.

8 DETERMINATION

To determine the water-soluble phosphoric acid, take a 100 cc. aliquot equivalent to 1 gram, add 20 cc. of the ammonium citrate under 2 (a), 50 cc. of ammonia, and 10 cc. of the magnesia mixture under 2 (b), and proceed as described under 3.

For the determination of both water-soluble and citrate-soluble phosphoric acid, introduce the filter containing the washed residue from the water-soluble phosphoric acid into a 150 cc. graduated flask with 60 cc. of ammonium citrate; digest for 1 hour with occasional agitation, allow to stand for 12 hours, dilute to 150 cc., mix and filter. Take 100 cc. of the filtrate and add to it 100 cc. of the solution prepared under 7. Carry out the precipitation in the united solutions as before, but without the addition of the ammonium citrate.

For separate determinations of water-soluble and citrate-soluble phosphoric acid, make separate precipitations in 100 cc. portions of both liquids. As it is important to have the liquid strongly ammoniacal, a volume of ammonia equal to one-third of the total volume is added in every case. On extraction of a superphosphate with water, a cloudy solution is often obtained owing to silicious matter in suspension in the wash waters. To avoid this it is advisable to add several drops of hydrochloric acid, dilute to the mark, and filter.

TABLE XV.—METHODS PRESCRIBED IN VARIOUS COUNTRIES FOR THE DETERMINATION OF PHOSPHORIC ACID.

Country	Total	Form of Phosphoric Acid			Free Alcohol
		Water-soluble	Citrate-soluble	Citric Acid-soluble	
Austria ¹ *	Citrate; Molybdate-magnesium	Citrate	Citrate	Citrate	Alcohol
Belgium ²	Citrate; Molybdate-magnesium	Citrate	Citrate	Molybdate-magnesium	
Czechoslovakia ³	Molybdate-magnesium		Lorenz-molybdate	Ferric Citrate; Lorenz-molybdate	Titration; Alcohol
Denmark ⁴	Molybdate-magnesium	Molybdate-magnesium	Citrate; Molybdate-magnesium	Molybdate-magnesium	
Hungary ⁵	Molybdate-magnesium	Citrate	Lorenz-molybdate	Ferric Citrate	
Italy ⁶	Citrate	Citrate	Citrate	Molybdate-magnesium	
Japan ⁷	Molybdate-magnesium	Citrate	Citrate	Molybdate-magnesium	
Norway ⁸	Citrate	Citrate	Citrate; Molybdate-magnesium	Molybdate-magnesium	
Russia ⁹	Woy-molybdate; Citrate; Lorenz-molybdate	Citrate	Citrate	Lorenz-molybdate	
Spain ¹⁰	Molybdate-magnesium	Citrate	Citrate	Molybdate-magnesium	
Sweden ¹¹	Citrate; Molybdate-magnesium	Molybdate-magnesium	Citrate; Molybdate-magnesium	Molybdate-magnesium; Ferric Citrate; Lorenz-molybdate	

* See p. 212 for references.

9 MECHANICAL ANALYSIS OF PHOSPHATES

The effectiveness of certain fertilizer materials increases with their degree of fineness, owing to the greater surface which they present to soil and root solvents.

For raw phosphates and phosphate slags in particular, the larger particles do not have any action on vegetation and should be regarded as inert and without value, hence the necessity of determining the quantity of these products remaining on the sieve, that is, in a non-utilizable condition.

The custom has been established of running the material through a No. 100 metallic wire sieve, of which the meshes have a uniform 0.17 mm. opening. Not more than 10 per cent of a raw phosphate ought to remain on the sieve, and not more than 20 per cent of a phosphatic slag.

OTHER COUNTRIES

The official methods prescribed for use in various other countries throughout the world are essentially the same as one or other of the methods already outlined as official for the United States, Great Britain, Germany, and France. The preceding table shows the particular methods prescribed for the determination of total, water-soluble, citrate-soluble and citric acid-soluble phosphoric acid in each of the countries listed.

¹ Methodenbuch. Verband der landwirtschaftlichen Versuchsstationen in Österreich. Vienna, 1913.

² Méthodes d'Analyse des Engrais. Ministère de l'Agriculture. Paris, 1897.

³ Private Communication, Ministry for Foreign Affairs. Prague, Jan. 4, 1920.

⁴ Fælles Arbejdsmetoder for Undersøgelser foretagne i Medfør af Lov om Handel med Gødningss - og Foderstoffer af 26. Marts 1898.

⁵ Private Communication. Royal Hungarian Ministry for Foreign Affairs. Budapest, Dec. 18, 1926.

⁶ Trattato di chimica analitica applicata, Vol. I. Rome, 1916.

⁷ Methods for the Analysis of Fertilizers. Agricultural Experimental Station. Department of Agriculture and Commerce.

⁸ Analyse av For - og Gjødselstoffer. Kristiania, 1924.

⁹ Private Communication. Scientific Institute of Fertilizers. Moscow, Oct. 12, 1928.

¹⁰ Procedimientos de Analisis de Abonos. Ministerio de Fomento. Madrid, 1919.

¹¹ Kungl. Lantbruksstyrelsens Kungörelse angående bestämmelser för undersökning vid de med statsmedel understödda kemiska stationerna. Stockholm, 1927.

CHAPTER V

NITROGEN

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Nitrogen is the most costly of the essential plant foods. The popular notion regarding its relatively great abundance is erroneous, since it forms only a minute part of the matter in and pertaining to the earth's crust. The great mass of nitrogen forming the bulk of the atmosphere is inert and useless for plant food; it is not until it is combined with other elements by electrical discharges, by the cyanamide or the direct synthetic ammonia process or by the action of certain micro-organisms that it assumes an agricultural value.

States of Nitrogen.—In this study of nitrogen as aggregated in a form suited for plant food, it may claim the attention of the analyst in the following forms:

(1) Organic compounds which contain nitrogen chiefly in the form of proteids. These include cottonseed meal, peanut meal, dried blood, packing house tankage, etc.

(2) Organic compounds originally of inferior quality which have been decomposed by superheated steam alone or with acids, for the purpose of rendering them more available to plants. Feathers, hair, leather and other trade wastes are treated in this way.

(3) Urea, salts of urea and cyanamide, the nitrogen of which may be partly changed to urea in the soil.

(4) Salts of ammonia, such as sulfate of ammonia, ammonium phosphate, ammonium nitrate, etc.

(5) Nitrates, such as nitrate of soda, nitrate of lime, and ammonium nitrate.

The analyst may be required to deal with the single material, or with mixtures of two or more of them, and he is usually required to estimate the total nitrogen. He may be requested to estimate the percentages of nitrogen present in mixtures as (a) in organic compounds and (b) in inorganic compounds, or it may be necessary to estimate the quantity of nitrogen present as (c) ammonium salts, and (d) nitrates, or other forms of combination. He may also be called on to decide whether the organic water-insoluble nitrogen is of good quality or not, and to estimate various constituents accompanying the nitrogenous compounds.

Seeds and Seed Residues.—The proteid matters in seeds and seed residues, after the extraction of the oil, are highly prized as nitrogenous fertilizers, either for direct application or for mixing. Typical of this class of substances is cottonseed meal, the residue left after the extraction of the oil from the meal, which is accomplished by pressure. The residual cakes still contain some oil, but nearly half their weight consists of nitrogenous compounds.

Cottonseed meal may contain 5.76-8 per cent nitrogen, though it rarely runs as high as 8 per cent. It contains 2-3 per cent of phosphoric acid, chiefly as an organic compound, phytin. It also contains 2-3 per cent of potash, mostly water soluble. Cottonseed meal is sold as 43 per cent protein cottonseed meal and 41 per cent protein cottonseed meal, and there are other grades in some states ranging down to 36 per cent protein. Cottonseed meal is an excellent feed as well as fertilizer, but owing to its high value as a protein feed it is ordinarily worth more as a feed than as a fertilizer, especially to the thrifty farmer, who can secure a large proportion of the fertilizing value in the droppings of the animal to which it is fed. This renders cottonseed meal an expensive source of fertilizer nitrogen, and although considerable quantities are still used for this purpose in the south, the amount tends to decrease. Sometimes, however, the price is sufficiently low to justify the extensive use of cottonseed meal as a fertilizer, and this is particularly the case in some sections of the south. Off grades of cottonseed meal, made from heated seed or that injured in quality during the process of manufacture and thus not well suited to feeding, are also available, particularly when excessive rainfall occurs during the season of picking the cotton. It is estimated by the United States Department of Agriculture that of the 2,840,000 tons of cottonseed meal produced in 1927, 450,000 tons was used as fertilizers, of which 120,000 tons was used in commercial mixtures and 330,000 tons directly by the farmers.

Linseed oil meal and peanut oil meal are similar to cottonseed meal and are sometimes used for fertilizer when they have been damaged in such a way as to render them unfit for feeding animals. Linseed oil meal is a by-product obtained from expressing the oil from flax seed, and peanut oil meal is a similar by-product obtained from peanuts. Cocoa meal, a by-product in the preparation of cocoa butter for use in bringing chocolate and cocoa to the legal content of fat, has also been used in small quantities as a fertilizer.

Dried Blood, Meat Meal and Digester Tankage.—The blood and scraps of meat, etc., from abattoirs afford sources of nitrogen in forms easily oxidized by the micro-organisms of the soil. Blood is prepared for use by drying and grinding. The intestines, scraps, and fragments of flesh resulting from trimming and cutting are placed in tanks and steamed under pressure to remove the fat. The dried and ground residue forms the tankage of commerce. The whole carcasses of animals condemned as unfit for food also are reduced to tankage. Dried blood is richer in proteid matter than any other substance in common use for fertilizing purposes. When it is in a completely dry state it may contain as much as 14 per cent of nitrogen, equivalent to nearly 88 per cent of proteid or albuminoid matter. Tankage is not so high in nitrogen as dried blood, but it contains enough to make it a highly desirable constituent of manures. Dried blood, tankage, and meat meal or meat scraps are now much more valuable for feeding animals than for use as a fertilizer. For this reason the quantities that can be purchased at prices that justify their use as fertilizers has steadily decreased, until at the present time in some sections of the country the supply is restricted to damaged or inferior materials, or to that in other respects not suitable for feeding. It is estimated (1927) that the meat packing industry produces 175,000 tons of tankage, 175,000 tons of cracklings and 4000 tons of dried blood, and that only about 5 per cent of the total goes into fertilizer.

Fish Scraps.—A large amount of nitrogen is received from sea fish. It is shown by Atwater that the edible part has an unusually high percentage of protein.¹ In round numbers about 75 per cent of the water-free edible parts of fish is composed of albuminoids. Some kinds of fish, as the menhaden, are taken chiefly for their oil and fertilizing value, but the residue after the oil has been extracted is rich in nitrogen. Squanto, an American Indian, first taught the early New England settlers the manurial value of fish.² Fish scraps are made from the residues of fish after the extraction of oil, or from bones and offal left in preparing fish for canning, drying, or otherwise for human food. Fish scrap of good quality is suitable for cattle food. When made of partly-decomposed material, or that otherwise of inferior quality, it is suitable only for fertilizer. The amount of fish scrap available for use as fertilizer is comparatively small.

¹ Report of Commissioner of Fish and Fisheries, 1888, 679.

² Goode, American Naturalist, 14, 473 (1880).

Bird Guano.—Immense quantities of nitrogen are secured, both from sea and land, by the various genera of birds. The well-known habit of birds in congregating in rookeries during the night and at certain seasons of the year tends to bring into a common receptacle the nitrogenous matters which they have gathered and which are deposited in their excrement and in the decay of their bodies. In former times the magnitude of these rookeries was probably much greater than now, but even at the present time they are of vast extent. The feathers of birds are particularly rich in nitrogen, and the nitrogenous content of the flesh of fowls is also high. The decay of the remains of birds, especially if it occurs where there is little leaching by water, tends to accumulate vast deposits of nitrogenous matter. Bird guano was formerly an important commercial fertilizer, as shown by the fact that fertilizer is still termed “guano” in some sections.

Bat Guano.—Bat guano is found in caves in Texas, parts of Mexico, Cuba, and other localities. Some of the caves are still inhabited by bats, and may produce 20-40 tons of guano a year. Bat guano appears to be liable to spontaneous combustion. If this occurs, the residue, bat-cave earth, is high in phosphates but low in nitrogen. All variations are found between the two extremes of fresh guano and bat-cave earth. Owing to the variations in deposits in different parts of the cave and from the surface downward, they are difficult to sample correctly, and therefore monetary losses have resulted from careless sampling. Some bat guano is also produced in roosts constructed to house bats kept to destroy mosquitoes.

Fresh bat guano may contain 10-12 per cent of nitrogen, and cave earth may contain 2 or 3 per cent nitrogen and 8 to 10 per cent phosphoric acid. Material taken from a cave may have a composition anywhere between the extremes mentioned. The guano high in nitrogen is usually found only in caves that still harbor colonies of bats.

Garbage Tankage.—The processed residues from household waste collected in cities is termed garbage tankage. It is derived from both animal and vegetable matter, and it varies in composition according to the manner of sorting the material before it is processed, as well as from summer to winter. Its nitrogen usually has a low availability.

Activated Sludge.—Sewage sludge separates in the process of purification of sewage, and in general it is of two types: (1) The suspended material is allowed to settle and to undergo a partial decomposition before the sludge is drawn off. This includes Imhoff sludge and similar sludges, in which the nitrogen has a low availability. At the present time this

sludge is disposed of in the most convenient way, little being utilized. (2) Air is pressed through the sewage, and vigorous bacterial action takes place. This sludge, known as activated, separates quickly, and is somewhat difficult to separate and dry. The city of Milwaukee is marketing dried activated sludge at the present time under the trade name Mil-organite. Chemical tests and pot and field experiments¹ show that this activated sludge has a good availability. It contains 2-2.6 per cent total phosphoric acid and 3.5-6 per cent nitrogen.

Imhoff Sewage Sludge.—Sewage sludge from Imhoff tanks and similar apparatus contains less nitrogen than does activated sludge, and the availability of the nitrogen is low, so that these sludges are not suitable for use in mixed fertilizers. Their composition is variable, but they contain much less nitrogen than activated sludge; in content of plant food and activity of the nitrogen they resemble barnyard manure more closely than commercial fertilizer, and thus they are suitable chiefly for local use. Imhoff sludges contain 0.5-2.5 per cent total phosphoric acid, with an average of about 1.5 per cent; 0.9-3 per cent nitrogen, average about 1.5 per cent; and 0.2-1.4 per cent potash, average about 0.3 per cent.

Sea Weeds.—Much of the waste nitrogen finds its way sooner or later to the sea, and is partly recovered in many forms. Sea weeds of all kinds contain organic nitrogen. Many years ago Forchhammer² pointed out the agricultural value of certain fucoids, and many other chemists have contributed important data in regard to the composition of these bodies. Jenkins³ showed from the analyses of several varieties of sea weeds that in the green state they are quite equal in fertilizing value to stall manure, and his data are fully corroborated by Goessman.⁴ Wheeler and Hartwell⁵ give the fullest and most systematic discussion that has been published of the agricultural value of this source of nitrogen. Sea weeds are too low in nitrogen to be used in commercial fertilizer.

Rough Ammoniates.—Hair, feathers, leather and similar materials are high in nitrogen, but they decay slowly in the soil and are generally recognized as unsuitable as such for use in commercial fertilizers. They are usually decomposed by treatment with steam or acids in order to render their nitrogen more soluble and available. As they are not used without such treatment, they are called *rough ammoniates* in the trade.

¹ *J. Am. Soc. Agron.*, **18**, 953 (1926).

² *J. prakt. Chem.*, **36**, 17, 385 (1845).

³ *Ann. Rpt. Connecticut Exp. Sta.*, **72** (1890).

⁴ *Ann. Rpt. Massachusetts Exp. Sta.*, **223** (1887).

Processed Tankage.—Processed tankages are made by the decomposition of leather, feathers, hair and other materials which contain nitrogen in inert forms. The decomposition is effected by steam under pressure, with or without acids. Part of the insoluble nitrogen is changed to salts of ammonia, part to water-soluble organic compounds, and a part remains in water-insoluble organic compounds which, however, may decompose in the soil more readily than the original material. Pot experiments have shown that the treatment increases the availability of the nitrogen. When properly made, processed tankages have a good availability in pot tests, and the insoluble organic nitrogenous material in many cases passes the A. O. A. C. test for activity. Processed tankages are sold under a number of trade names.

Base Goods.—Rough ammoniates may also be processed during the manufacture of superphosphate, with the production of base goods. They are mixed with the phosphate rock before the addition of sulfuric acid and undergo a decomposition through the action of the acid and the heat generated by the reaction. The analysis of a sample of base goods prepared in this way is as follows:¹ Total nitrogen 1.75 per cent; nitrogen in ammonium salts 0.25 per cent; nitrogen in organic forms 1.50 per cent; water-soluble organic nitrogen 1.01 per cent; water-insoluble organic nitrogen 0.49 per cent. Nearly 75 per cent of the organic nitrogen has been made water-soluble. Base goods may also be prepared by mixing ammonium sulfate or other materials with superphosphate; the mixture is allowed to cure or harden, and then ground, the object being to have a base to mix with other materials to produce a fertilizer of the desired grade, of good physical condition, and one that does not harden in the sacks.

Proteid Fertilizer Nitrogen Limited in Amount.—Organic nitrogen in the form of cottonseed meal, tankage, fish scrap and similar proteid materials is limited in amount, and the supply is decreasing owing to the increasingly extensive use of these materials for feeding. According to H. R. Bates,² the supply from all sources, production and importation, is between 45,000 and 50,000 tons of organic nitrogen, and there is no prospect of increasing this amount. The estimated tonnage of nitrogen consumed as fertilizer in the United States was 380,000 tons in 1929. As the tonnage increases, the proportion of organic nitrogen of the kinds

¹ *J. Ind. Eng. Chem.*, **7**, 671 (1915).

² *Ind. Eng. Chem.*, **20**, 1135 (1928).

mentioned is sure to decrease. In other words, the nitrogen for fertilizer must be derived to an increasingly greater extent from inorganic sources.

The differences in the prices of organic proteid nitrogenous fertilizer material and other nitrogenous materials will depend on the demand. At present nitrogen in organic materials sells at a higher price than that in inorganic materials, and it is a question if the difference in price is justified by the agricultural value. This is a situation that requires careful handling; otherwise the agricultural chemist may be responsible for the farmer paying too much for the nitrogen in his fertilizer.

Urea and calcium cyanamide, which are classed as organic and can be produced synthetically, are not included in this consideration. They are simple non-proteid nitrogenous compounds, more closely related agriculturally to inorganic compounds than to organic materials similar to proteids.

Soils Impregnated with Nitrogen.—While consideration is given only to deposits of nitrates which are of sufficient value to bear transportation or to warrant their concentration or leaching, yet much interest attaches to the formation of nitrates in the soil even when they are not of commercial importance. In many of the soils of tropical regions not subject to heavy rain, the accumulation of nitrates is very great. Müntz and Marcano investigated many of the soils to which attention was called first by Humboldt and Boussingault,¹ and they state that these soils are incomparably richer in nitrates than the most fertile soils of Europe. The samples which they examined were collected from different parts of Venezuela and from the valley of the Orinoco, as well as on the shore of the Caribbean Sea. The nitrated soils in this region of South America cover large surfaces. Their composition is variable, but carbonate and phosphate of lime are found, as well as organic nitrogenous material. The nitric acid is always combined with lime. In some of the soils as high as 30 per cent of nitrate of lime has been found. Nitrification of organic material takes place rapidly the year round in this tropical region. These soils are always abundant around caves that serve as the refuge of birds and bats, as described by Humboldt. Large quantities of this guano are also formed from the debris of insects, fragments of elytra, scales of the wings of butterflies, etc. The nitrification that occurs in these deposits has been found to extend its products to a distance of several kilometers through the soil. In some places the quantity of the nitrate of lime is so great that soils are converted into a plastic paste by this deliquescent salt.

¹ *Compt. rend.*, **101**, 65 (1885).

Deposits of Nitrates in Chile.—The existence of nitrate deposits in Chile has long been known.¹ The old Indian laws originally prohibited the collection of the salt; nevertheless, it was secretly collected and sold. Until 1821 soda saltpeter was not known in Europe except as a laboratory product. About this time the naturalist, Mariano de Rivero, found on the Pacific coast, in the Province of Tarapaca, immense new deposits of the salt. Later it was found in equal abundance in the Territory of Antofagasta, and, further to the south, in the desert of Atacama, which forms the Department of Taltal.

The theory of Müntz and Marcano in regard to the nitrates of soils in the neighborhood of caves is probably a correct one, but there are many objections to accepting it to explain the great deposits of nitrate of soda which occur in Chile and in other parts of the world. Another point which must be considered also is that the process of nitrification can not be going on now with the same vigor as formerly. Some moisture is necessary since the nitrifying ferment does not act in perfectly dry soil, and in many localities in Chile, where the nitrates are found, it is too dry to suppose that any active nitrification is taking place.

According to Pissis, these deposits are of very ancient origin, the result of the decomposition of feldspathic rocks, the bases thus produced gradually becoming united with the nitric acid provided from the air.²

According to the theory of Nöllner, these deposits are of more modern origin and due to the decomposition of marine vegetation.³ Continuous solution of soils gives rise to the formation of great lakes of saturated water, in which occurs the development of much marine vegetation. When this water evaporates, due to geologic isolation, the decomposition of nitrogenous organic matter causes generation of nitric acid, which, coming in contact with the calcareous rocks, attacks them, forming nitrate of calcium. In the presence of sulfate of sodium the nitrate of calcium gives rise to a double decomposition which produces nitrate of sodium and sulfate of calcium.

The fact that iodine is found in greater or less quantity in Chile salt-peter is one of the chief supports of this hypothesis of marine origin, inasmuch as iodine is always found in marine and not in terrestrial plants. It must also be taken into consideration that these deposits of nitrate of soda contain neither shells nor fossils, nor do they contain any phosphate

¹ *J. Royal Agr. Soc.*, **12**, 349 (1852).

² Fuchs and de Launay, *Traité des Gites minéraux*, **1**, 425 (1893).

³ Le Feuvre and Dagnino, *El Salitre de Chile*, 1893, 12.

of lime. The theory, therefore, that they are due to animal origin is scarcely tenable.

Nitrate deposits extending over 30 square miles and varying in thickness from 1 to 10 feet were discovered in the U. S. of Columbia.¹ They consist of a mixture of sodium nitrate, sodium chloride, calcium sulfate, aluminum sulfate and insoluble silica, and contain from 1 to 13.5 per cent of nitrate.

Niter Deposits, California and Arizona.—Many of the conditions which favor the deposition of niter in the soil are found in Southern California and Arizona. The California State Mining Bureau made investigations of such deposits in Southern California in 1902. Nearly all of them are found in the northern part of San Bernardino County, particularly along the shore lines, or old beaches, that mark the boundry of Death Valley as it doubtless appeared during the Eocene period. It was found that the average composition of 104 samples of caliche, taken from as many different claims, was 9.54 per cent of niter. About 35,000 acres were examined, and it was estimated that the deposit approximated 22,000,000 tons of nitrate of soda. From a commercial point of view these niter beds of California are of little importance. The amount of niter is comparatively small, and the cost of transportation practically excludes the product from the markets of the world.

UTILIZATION OF THE NITROGEN OF THE AIR

The nitrogen of the air may be utilized as a fertilizer material, and two processes are available at present for this purpose. One, the agricultural method, is by life processes, that is the nitrogen is fixed by the bacteria which live in nodules on the roots of legumes, or by bacteria living in the soil. Although the rôle of legumes as soil builders has been known for centuries, the means by which the work is accomplished was not discovered until 1882, by Hillreigel. The products of the life processes are not directly available for use in fertilizer. The other, the industrial method, is by processes for causing the free nitrogen of the air to combine with other elements. The products of this method are available for use in commercial fertilizer, for industrial use, and for other purposes.

Industrial Processes for Fixation of Nitrogen.—The industrial processes for the fixation of free atmospheric nitrogen may be classified into three

¹ Wiley, Presidential Address, *J. Am. Chem. Soc.*, **16**, 20 (1894).

groups, which differ in the method of manipulation and in the first product formed:

- (a) The arc process, or the direct combination of nitrogen with oxygen, producing nitric acid and nitrates.
- (b) The cyanamide process, or the combination of nitrogen with calcium carbide to form calcium cyanamide, from which other nitrogenous compounds may be secured.
- (c) The ammonia process, or the direct combination of nitrogen and hydrogen to form ammonia and salts of ammonia. The ammonia may be oxidized to form nitrates, or be converted into urea.

The industrial fixation of nitrogen¹ is of recent development, as is shown by Table I.

TABLE I.—WORLD PRODUCTION OF INORGANIC NITROGEN
(Net tons of nitrogen per year)

	1909	1913	1917	Year ending 5-31-1924	Year ending 5-31-1928	Per cent of total* for 1928
By-product ammonia	233,200	377,300	400,400	346,200	430,600	23.6
Chilean nitrate	330,000	429,000	413,200	372,200	429,000	23.6
Arc process	3,300	19,800	33,000	33,000	33,000	1.8
Cyanamide process	2,750	66,000	220,000	136,400	250,000	13.7
Direct synthesis process	0	7,700	125,000	275,100	680,000	37.3
Total	569,250	899,800	1,205,600	1,162,900	1,822,600	100.00

The nitrogen fixation capacity of the world at the end of 1929 was distributed among about 111 plants. The location and process are shown in Table II. It will be noted that Germany produces fully one-half of the total capacity and it is also of interest that two-thirds of Germany's production is in one plant, the direct synthetic ammonia plant at Merseburg.

It will be noted that the arc process, the oldest of the three, is least used, while the direct synthetic ammonia process, the youngest of the three, is used to the greatest extent. Various causes have contributed to the success or failure of the different processes. One of these is power consumption. The arc process uses 60,000 kilowatt hours per ton of nitrogen fixed; the cyanamide process, 12,000-14,000 and the most commonly used modification of the direct synthetic process, only 4,000 kilowatt hours. This has had the effect of limiting the arc process to localities

¹ The section pertaining to the fixation of nitrogen was written by P. E. Howard, Chemical Engineer, Fixed Nitrogen Laboratory, U. S. Department of Agriculture, Washington, D. C.

TABLE II.—NITROGEN FIXATION CAPACITY OF THE WORLD FOR 1929.
(Net tons of nitrogen per year)

	Arc process	Cyanamide process	Direct synthetic ammonia process	Total
Belgium			46,500	46,500
Canada		50,000		50,000
Czechoslovakia		6,000	12,400	18,400
England			58,000	58,000
France	1,200	53,000	114,050	168,300
Germany	4,500	114,000	795,000	913,500
Italy		21,900	58,000	79,900
Japan		63,600	33,700	97,300
Jugoslavia		14,000		14,000
Netherlands			11,000	11,000
Norway	31,000	15,000	54,000	100,000
Poland		30,000	6,000	36,000
Russia			7,000	7,000
Roumania		5,000		5,000
Spain			8,350	8,350
Sweden		6,000	2,000	8,000
Switzerland		5,000	7,000	12,000
United States		40,000	128,800	168,800
	36,700	423,500	1,341,800	1,802,050

of extremely cheap water power, as in Norway, where power has been available at a cost of only \$4 or \$5 per horsepower year. In fact, it is only in Norway that the arc process has attained any considerable success. The power requirements of the cyanamide process are also high enough to make rather cheap power essential. On the other hand, the direct synthetic process is not dependent on special power conditions of any kind. The first product of the arc process is weak (30 per cent) nitric acid; with the cyanamide process it is crude calcium cyanamide; and with the direct synthetic ammonia process the product is high-grade liquid ammonia or aqua ammonia.

In the United States nitrogen fixation has grown steadily, but at a slow rate until recently. Rapid progress in industrial development has been accomplished during 1928 and 1929, as will be seen from Table III, which shows domestic nitrogen production including by-product ammonia for each year since 1919, when production of fixed atmospheric nitrogen began in this country.

TABLE III.—NITROGENOUS MATERIAL PRODUCED IN THE UNITED STATES.
(Net tons nitrogen)

	By-product ammonia	Air nitrogen	Total
1919	85,000	276	85,276
1920	104,000	270	104,270
1921	73,600	200	73,800
1922	97,500	740	98,240
1923	123,500	5,910	129,410
1924	116,600	11,110	127,710
1925	136,000	13,050	149,050
1926	146,500	14,000	160,500
1927	152,000	18,000	170,000
1928	170,000	26,000	196,000
1929	187,000	84,000	271,000

DESCRIPTION OF FIXATION PROCESSES

Arc Process.—The commercial arc process for the fixation of nitrogen consists in heating air to a high temperature by passing it through an electric arc. Under these conditions a small percentage of the nitrogen is oxidized to nitric oxide: $N_2 + O_2 = 2NO$. The oxide thus formed is preserved by cooling so quickly that its decomposition, which proceeds rapidly at high temperature but only slowly at lower temperatures, is practically stopped. On further cooling the dioxide is formed by oxidation, which takes place spontaneously: $2NO + O_2 = 2NO_2$. The gas is further cooled and passed to absorption tubes, where in contact with water the formation of the nitric acid is completed by the following reversible reactions: $2NO_2 + H_2O = HNO_2 + HNO_3$; $3HNO_2 = HNO_3 + 2NO + H_2O$; or $3NO_2 + H_2O = 2HNO_3 + NO$. The nitric oxide so formed reacts again with oxygen, and the cycle is completed again and again until the oxide in the exhaust gases is reduced to an allowable amount. Alkaline solutions are frequently used to complete the absorption.

The gases leave the furnace at 900°-1100° C. The second step in the oxidation begins at 620° C., but it is completed at or below 50° C. in the absorption towers.

The concentration of the oxide in the gas going to the absorption towers rarely exceeds 2 per cent and this limits the strength of the acid produced to about 30 per cent. This is a satisfactory acid for the manufacture of ammonium nitrate, sodium nitrate or calcium nitrate by neutralization with ammonia, limestone or soda ash, respectively. However, the low concentration is a drawback when it is desired to produce strong nitric acid by direct concentration.

A typical Birkeland-Eyde furnace uses 4,000 kilowatts at 10,000 volts. In this furnace an alternating current arc is maintained between water-cooled copper electrodes, which are placed between the poles of an electromagnet in such a way that the direction of the arc is at right angles to that of the constant magnetic field. The magnetic field causes the arc to spread in a semicircular form, first in one direction and then in the opposite direction, according to the direction of the current in the arc. As the arc elongates under the action of the magnetic field and recedes along the electrodes, its electrical resistance increases, causing the potential between the furnace electrodes to rise. When this potential has risen high enough a new arc will strike across the short gap at the ends of the electrodes, thus leading to the extinction of the long arc. This process repeats so rapidly that the arc appears as a thin disk in a plane at right angles to the line joining the poles of the magnet.

In spite of much effort to improve furnace efficiency and to recover heat from the hot gases, the process is still extremely wasteful of energy; 60,000 kilowatt hours are required per ton of nitrogen fixed.

A typical absorption system consists of several towers as large as 75 feet high and 20 feet in diameter, made of brick or granite packed with broken quartz, etc., to give contact surface for the absorbing water or alkaline solution.

Cyanamide Process.—There are three principal steps in the cyanamide process proper—the production of calcium carbide—which involves, first, the burning of limestone to lime, and then the fusing of the lime with coke in an electric furnace; the isolation of nitrogen from the air in a rather pure state; and, finally, the treatment of the finely powdered highly heated carbide with nitrogen, resulting in the fixation of nitrogen according to the equation: $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$.

The raw materials for the process are limestone and some form of carbon, either charcoal, anthracite coal, or coke, the latter being generally used. The nitrogen is ordinarily obtained by the fractional distillation of liquid air.

The nitrification of the carbide, to which some material such as calcium fluoride has been added to speed up the reaction, is carried out at a temperature of 1100° - 1200° C. in an oven so arranged as to allow free access of the nitrogen to the carbide, conserve the heat of the reaction and allow for heating electrically to start the reaction, which is exothermic and able to maintain its own temperature when once well under way. At the end

of the reaction the oven, which is filled with finely pulverized carbide, yields a solid ingot of bluish-black crude calcium cyanamide.

This ingot is crushed and pulverized and treated with a small quantity of water, with constant stirring, to destroy residual calcium carbide left by incomplete nitrification. The product, which is variously termed lime-nitrogen, nitrolim, calcium cyanamide, cyanamide, or cyanamid, is now ready for the autoclaves if it is to be converted into ammonia or to be prepared for use as fertilizer by treatment with a small quantity of oil to settle the dust or by granulation. In either case steps are taken to insure complete hydration of the carbide.

A typical cyanamide contains 21 per cent nitrogen; the analysis is approximately as follows:

	<u>Per cent</u>
Calcium cyanamide	63.5
Calcium carbonate	2.0
Calcium hydroxide	17.0
Calcium sulfide	1.0
Free carbon	11.0
Iron and alumina	2.0
Silica	2.0
Combined water	1.5
Free moisture	1.0

If proper precautions are observed, cyanamide may be applied to the soil directly or mixed in limited quantity with other materials to make complete fertilizers.¹ It is a cheap material and when used under favorable conditions it gives excellent results. It has certain objectionable properties, however, which make it necessary to follow carefully prescribed rules for its use if ill effects are to be avoided and the best result obtained. By far the largest part of the world's output of this material is applied to the soil separately.

Direct Synthetic Ammonia Process.—The reaction for ammonia synthesis is as follows: $N_2 + 3H_2 = 2NH_3$. Commercially this reaction is carried out at high pressure, 100-1000 atmospheres and at temperatures of 450°-700° C. in the presence of a catalyst. Various materials catalyze this reaction. A catalyst developed by the Fixed Nitrogen Research Laboratory, United States Department of Agriculture, and now in general use in the industry, consists chiefly of iron initially as the oxide with small quantities of potassium and aluminum oxide known as promoters. The nitrogen hydrogen mixture is obtained in various ways and this is an

¹ Allison, U. S. Dept. Agr. Circ. 64.

important step in the process since the cost of the hydrogen often amounts to more than half the total cost of the ammonia. Hydrogen for use in this process is obtained (1) from the water gas process with producer gas added to furnish the nitrogen; (2) from electrolysis of water; (3) as a by-product in the manufacture of chlorine and of sodium; and (4) from coke-oven gas by liquefaction and absorption methods. In the first case the three to one mixture is obtained directly, the nitrogen accompanying the hydrogen through the purification process as a by-product. Nitrogen is obtained for use with straight hydrogen by burning the oxygen from air with hydrogen or by liquid air separation. In one process for recovery of coke-oven hydrogen the final step in purification is accomplished by scrubbing with liquid nitrogen to remove carbon monoxide, and in this case the hydrogen picks up the required nitrogen from the liquid nitrogen. In the case of water-gas production large quantities of carbon monoxide are produced along with the hydrogen in the gas machine and must be removed or converted to hydrogen in a converter with the aid of a catalyst, by the reaction: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$; the carbon dioxide is then scrubbed out with water under pressure as the first step of the purification process which produces by scrubbing with cuprous ammonium carbonate or formate and caustic, etc., a gas practically free from carbon dioxide, carbon monoxide, oxygen, and moisture.

During its passage through the ammonia catalyst bomb a part of the gas mixture is converted into ammonia, the percentage of conversion depending on pressure, temperature, activity of the catalyst, and time of contact. The ammonia is removed from the gas after cooling by liquefaction or absorption in water, and the residual gas is returned to the stream going to the converter. The ammonia equilibrium reaches 52 per cent at 500 atmospheres pressure and 400°C ., and even higher conversion is possible at higher pressures or lower temperature.¹

Nitrogen Conversion Products.—During the year 1909, 58 per cent of the world's inorganic nitrogen was produced as Chilean nitrate of soda and 0.6 per cent as arc process nitrate. During 1929 less than 25 per cent was from these sources; 75 per cent was ammonia or cyanamide, a part of which was converted to ammonia. This shift has had a marked effect on comparative prices. In 1909 the price of nitrogen in ammonium sulfate and in Chilean nitrate was practically the same. In 1929 ammonium sulfate was quoted at the same price per ton as Chilean nitrate in spite of the fact that it contains one-third more nitrogen. The abundant

¹ Ordnance Document No. 2041.

supply of cyanamide and ammonia and the resulting low price has encouraged their conversion into other forms and into materials in greater demand in agriculture and industry.

Ammonia from Cyanamide.—The production of ammonia from cyanamide is a comparatively simple operation, consisting in the treatment of cyanamide with water and steam in an autoclave. It was very largely for this reason that the cyanamide process assumed its importance during the World War as a method of fixing nitrogen for use in the production of military explosives.

The process as actually carried out involves the following steps: (1) The elimination of free carbide by hydration; (2) the treatment of the hydrated cyanamide with water and steam in an autoclave; (3) the separation of the ammonia from the steam-ammonia mixture; (4) the treatment of the autoclave sludge to recover the alkali that had been added as soda ash in making up the charge; and (5) the disposal of the sludge.

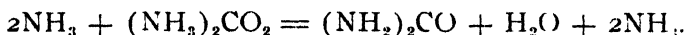
The course of the reaction, which is assisted by the presence of alkali, is not fully understood. However, the net result of the chemical changes involved in treatment are quite accurately represented by the equation $\text{CaCN}_2 + 3\text{H}_2\text{O} = 2\text{NH}_3 + \text{CaCO}_3$. The conversion is practically complete in such autoclaves as those at United States Nitrate Plant No. 2, which are 21 feet high, 6 feet in diameter and constructed to operate at pressures up to 300 pounds per square inch. In operating these autoclaves about 19,000 pounds of filtrate liquor from a previous operation are introduced with 8,000 pounds of cyanamide and enough soda ash to bring the alkali concentration to the equivalent of 3 per cent sodium hydroxide.

Cyanide is produced by the American Cyanamid Company from crude calcium cyanamide by strongly heating the latter in the presence of free carbon with a flux such as sodium chloride. It is believed that the reaction is as follows: $\text{CaCN}_2 + \text{C} = \text{Ca}(\text{CN})_2$. This process is commercially important as a source of cyanide for fumigation and for metallurgy.

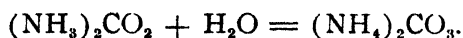
Ammonia oxidation is in successful and widespread use. By this process ammonia is converted into nitric acid for use in manufacturing operations such as explosive production, sulfuric acid manufacture, etc., or for use in making salts such as ammonium nitrate, calcium nitrate and sodium nitrate. The reactions involved in this process are as follows: $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$; $2\text{NO} + \text{O}_2 = 2\text{NO}_2$; and $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$. The first reaction takes place only at a high temperature (around 700°-1000° C.) and in the presence of a

catalyst. Platinum gauze has been used extensively, but many other materials have been suggested and very good results have been obtained with some of them. Ordinarily ammonia-air mixtures containing 9-10 per cent of ammonia are used. The second reaction begins as the gas cools and continues throughout the system or until all the oxide is converted into nitric acid. The third reaction takes place in the absorption system where the gas is circulating in contact with water and dilute nitric acid. The process is ordinarily operated at atmospheric pressure and yields acid containing about 50 per cent HNO_3 , which is entirely satisfactory for use in the production of salts. However, if *concentrated acid* is required, as in explosives manufacture, it is advantageous to carry out the whole process under pressure, in which case acid containing about 70 per cent HNO_3 can be obtained as the first product. When the process is used in connection with the chamber sulfuric acid process only the first two reactions are used, the gas being conveyed directly to the chambers from the converter. The ammonia oxidation process is rapidly replacing the old retort process, which uses nitrate of soda and sulfuric acid for nitric acid production. The transition, which is nearly complete in Europe, is well under way in the United States and it seems probable that the retort process will be little used in the future.

Urea is a desirable fertilizer material and has promising industrial uses. It can be made from either cyanamide or from ammonia. In the ammonia process the only additional raw material required is carbon dioxide, which is the main by-product of the direct synthetic ammonia process. It is carried out by pumping ammonia and carbon dioxide into a converter at about 100 atmospheres pressure. These materials combine immediately to form ammonium carbamate, according to the following reaction: $\text{CO}_2 + \text{NH}_3 = (\text{NH}_4)_2\text{CO}_2$. In the presence of excess ammonia and at the elevated temperature of the converter, water splits off from the carbamate with the formation of urea.



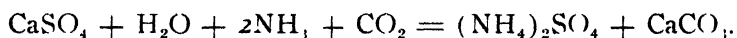
The yield is limited by the unavoidable reaction:



The product containing urea, carbamate and carbonate is distilled to break up the carbamate and carbonate but at a temperature insufficient to destroy the urea. The ammonia and carbon dioxide so recovered are returned to the process.

Urea and *Calurea*, a double salt made by combining urea and calcium nitrate in solution, are used to some extent as fertilizer materials. They are both very concentrated products, urea having about 46 per cent nitrogen and calurea about 34 per cent.

Ammonium Sulfate is undoubtedly the most important nitrogenous fertilizer material, the annual world production being about 4,500,000 tons. It has long been made by neutralizing sulfuric acid with ammonia in a container called a saturator, under such conditions that the salt crystallizes out as formed. It is separated from the mother liquor, washed and dried. No evaporation is necessary. With the coming of the direct synthetic ammonia process and its by-product, carbon dioxide, another process has come into use in Europe. This process consists in subjecting a slurry of finely pulverized gypsum and water to the action of ammonia and carbon dioxide, the reaction being essentially as follows:



Commercial ammonium sulfate contains 20.6 per cent nitrogen.

Ammonium Chloride is produced from ammonia, carbon dioxide and common salt in water solution by the Solvay soda process used primarily for the production of soda ash, sodium carbonate. It contains 24 per cent nitrogen. It is not used extensively in fertilizer.

Ammonium Sulfate-nitrate, known also as leunasalpeter, is a double salt of ammonium sulfate and ammonium nitrate. This salt is used extensively in fertilizer and was imported to the United States to the extent of 91,608 tons in 1928.

Monoammonium Phosphate and *Diammonium Phosphate* are manufactured for fertilizer use by adding ammonia to crude phosphoric acid. The ammophos of the American Cyanamid Co., and the nitrophoska of the German I. G. contain one of these salts. These are concentrated fertilizers. There are two grades of ammophos, containing 20 per cent nitrogen and 20 per cent P_2O_5 , and 13 per cent nitrogen and 48 per cent P_2O_5 , respectively. Nitrophoska No. 1 contains 15 per cent nitrogen, 30 per cent P_2O_5 , and 15 per cent K_2O .

Calcium Nitrate, *Sodium Nitrate*, and *Ammonium Nitrate* containing 15.5 per cent, 16 per cent and 34.5 per cent nitrogen, respectively, are made by neutralizing nitric acid with limestone, soda ash or ammonia gas. They are all important commercially. *Potassium nitrate* and *potassium ammonium nitrate* are promising materials of less commercial importance at this time.

Direct Use of Liquid Ammonia in Fertilizer Manufacture.—Some fertilizer manufacturers purchase liquid ammonia in tank cars and mix it, as a gas or dissolved in water, with superphosphate. Only a small amount may be used in this way, as an excess will revert part of the available phosphoric acid. This treatment removes the free acid in the superphosphate. The method requires special equipment.

Use of Term "Nitrogen."—In 1927 the National Fertilizer Conference recommended that nitrogen only be used in referring to fertilizer and the use of the term ammonia be discontinued. The recommendation was made to obviate the prevailing confusion due to the use of the term nitrogen in some parts of the country, ammonia in others, and both at times, and was based upon the practical reason that nitrogen was required by the laws of most of the states, while ammonia was only permitted. This action of the First National Fertilizer Conference was endorsed by the National Fertilizer Association, the Association of Official Agricultural Chemists, the American Society of Agronomy, and other organizations. It appears that in a short time the use of the term ammonia in grades and analyses will be eliminated, existing confusion will be cleared up, and national and international uniformity, based on the use of the term nitrogen, will prevail.

METHODS FOR DETERMINATION OF TOTAL NITROGEN

There are three direct methods of determining the total nitrogen content of fertilizers. (1) The nitrogen is secured in a gaseous form, the volume is measured, under standard conditions, and the weight of nitrogen is computed. This process, first perfected by Dumas, whose name it bears, and commonly known as the absolute method, has practically passed out of use. It consists of the combustion of the nitrogenous body in the presence of copper oxide. The nitrogen, by reason of its inertness, is left in a gaseous state after the oxidation of the carbon and hydrogen. (2) The nitrogen is converted into ammonia, which is volatilized and absorbed by an excess of standard acid, and the residue is determined by subsequent titration with a standard alkali. In one step of this procedure ammonia is directly produced by dry combustion of the organic nitrogenous compound with an alkali; in the other, ammonium sulfate is produced by moist combustion with sulfuric acid, the salt thus formed is subsequently distilled with an alkali, and the ammonia is estimated as described previously. Nitric nitrogen may be reduced to ammonia by nascent hydrogen either in an acid or an alkaline solution. (3) Nitric

nitrogen is estimated by colorimetric methods. These processes have little practical value in connection with the analysis of commercial fertilizers; their chief use is in the detection and estimation of extremely minute quantities of nitrites and nitrates. In the following paragraphs will be given the standard methods for the determination of nitrogen in practical work with fertilizers and fertilizing materials.

Official Methods.—The methods adopted by the Association of Official Agricultural Chemists should be strictly followed, especially for official work, and when comparison with other data is made. The latest reports should be consulted because these methods are constantly undergoing study and revision by the referees of the Association.

Gasometric Estimation by Combustion with Copper Oxide.—By the combustion in copper oxide of a substance containing nitrogen and the conduction of the products of the oxidation over red-hot copper oxide and metallic copper, all the nitrogen present in whatever form will be obtained in a free state and can subsequently be measured as a gas. The air originally present in all parts of the apparatus must first be removed by a mercury pump, by carbon dioxide, or by a combination of the two, the residual carbon dioxide being absorbed by a solution of caustic alkali. Great delicacy of manipulation is necessary to secure a perfect vacuum; as a rule a small quantity of gas other than nitrogen may be measured, so that the results of the analyses are often a trifle too high. The former official gasometric method may be used for the determination of nitrogen in any form of combination and also for special work. In 1927 it was removed from the official methods, but it may be found in both the 1920 and 1925 editions of *Methods of Analysis, A. O. A. C.* It has practically gone out of use owing to the precautions necessary to take to obtain complete combustion and to avoid a consequent deficit in the volume of nitrogen obtained, but especially on account of the time required and the inability to run a number of determinations at a time. Official chemists rarely use it even for control work on samples sent out for comparative analysis.

Soda-Lime Process.—This process, originally perfected by Varrentrap and Will and improved by Peligot, was used extensively by analysts until about 1890 for the determination of nitrogen not existing in the nitric form. It is based on the principle that when nitrogen exists as a salt of ammonia, as an amide, or as proteid matter, it is converted into gaseous ammonia by combustion with an alkali. This ammonia can be carried into a standard solution of acid by a stream of gas free of ammonia and

the excess of acid remaining after the combustion is complete can be determined by titration against a standard alkali solution. The results, under proper conditions, are accurate even when a small quantity of nitric nitrogen is present. When, however, there is any considerable quantity of nitric nitrogen in the sample, the method becomes inaccurate by reason of non-reduction of some of the nitrogen oxides produced by the combustion.

In bodies very high in nitrogen, such as urea, all the nitrogen is not changed into ammonia at the commencement of the combustion. A portion of it may unite with a part of the carbon to form cyanogen, which may unite with the soda to form sodium cyanide. With an excess of alkali, however, and prolonged combustion this product will finally be decomposed and all the nitrogen will be secured as ammonia.

The nascent hydrogen that unites with the nitrogen during the combustion is derived from the organic matter, which always contains enough carbon to decompose the water formed. While at first the hydrogen may unite with the oxygen, it again becomes free by the oxidation of the carbon, and in this condition it unites with the nascent nitrogen to form ammonia. In addition to carbon dioxide, ammonia and free hydrogen there may also be found among the products of combustion marsh and olefiant gases and other hydrocarbon compounds which dilute, to a greater or less extent, the ammonia formed and help to carry it out of the combustion tube and into the standard acid.

The Combustion Method for Ammonia.—*Reagents and Apparatus.*—(1) *Standard solutions and indicator.*—Same as for the Kjeldahl method.

(2) *Dry granulated soda-lime.*—Fine enough to pass a 2.5 mm. sieve.

(3) *Soda-lime*—Fine enough to pass a 1.25 mm. sieve.

Prepared easily and cheaply by slaking 2.5 parts of quicklime with a strong solution of 1 part of commercial caustic soda, taking care to have enough water in the solution to slake the lime. Dry the mixture and heat in an iron pot to incipient fusion; when cold, grind and sift as directed above.

(4) *Sodium carbonate and lime or slaked lime.*—Instead of soda-lime, use a mixture of sodium and calcium carbonate, or slaked lime.

(5) *Asbestos.*—Ignite and keep in a glass-stoppered bottle.

(6) *Combustion tubes.*—About 40 cm. long and with an internal diameter of 12 mm., drawn out to a closed point at one end.

(7) *U-tubes.*—Large-bulbed U-tubes with glass stopcock, or Will's tubes with four bulbs.

Manipulation.—Powder the substance to be analyzed finely enough to pass through a sieve of 1 mm. mesh and use 0.7-1.4 gram, according to the quantity of nitrogen present. Put a small loose plug of asbestos into the closed end of the combustion tube and upon it to the depth of about 4 cm., fine soda-lime. Mix the

substance to be analyzed in a porcelain dish or mortar thoroughly but quickly, with enough fine soda-lime to fill approximately 16 cm. of the tube, or about 40 times as much soda-lime as substance, and put the mixture into the combustion tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda-lime, which is to be put in on top of the mixture. Fill the rest of the tube to within about 5 cm. of the end with granulated soda-lime, making it as compact as possible by tapping the tube gently while holding in a nearly upright position during the filling. The layer of granulated soda-lime should not be less than 12 cm. Lastly, put in a plug of asbestos about 2 cm long, press rather tightly, and wipe out the end of the tube to free it from adhering particles.

Connect the tube by means of a well-fitting rubber stopper or cork with the U-tube or Will's bulb, containing 10 cc. of standard acid, and so adjust it in the combustion furnace that the end of the tube projects about 4 cm. from the furnace, suitably supporting the U-tube or Will's bulb. Heat the portion of the tube containing the granulated soda-lime to a moderate redness; then extend the heat gradually through the portion containing the substance so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly. Continue the combustion until gases have ceased bubbling through the acid in the bulbs and the mixture of substance and soda-lime has become white, or nearly so, which shows that the combustion is finished. The combustion should occupy about 45 minutes, but not more than one hour. Extinguish the burners and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for 2-3 minutes to bring all the ammonia into the acid. Disconnect the tube, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion keep the end of the tube projecting from the furnace heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion tube.

It is found advantageous to attach a Bunsen valve to the exit tube, which allows the evolved gases to pass out freely but prevents a violent sucking back in case of a sudden condensation of steam in the bulbs.

It often happens, especially in the the combustion of animal products, such as tankage and fish scrap, that the acid receiving the ammonia is deeply colored by the condensation of some of the other products of combustion. This coloration interferes seriously with the delicacy of the indicator used to determine the end of the reaction. In this case the liquid may be mixed with an alkali and distilled, and the ammonia secured in a fresh portion of the standard acid as in the moist combustion process to be described.

General Considerations.—(1) *Preparation of the Sample.*—In the soda-lime method it is of great importance that the organic substances be in a fine state of subdivision so as to admit of intimate mixture with the alkali. In cases where fragments of hoof, horn, hair, or similar substances

are to be prepared for combustion, it is advisable first to decompose them by heating with a small quantity of sulfuric acid. The excess of acid may be neutralized with marble dust and the resulting mixture dried, rubbed to a fine powder, and mixed with the soda-lime in the usual way. Care must be taken not to lose any of the ammonia from the sulfate, which may possibly be formed, in mixing with the soda-lime in filling the tube.

(2) *Purity of Soda-Lime.*—The soda-lime used must be entirely free of nitrogenous compounds, and blank combustions should be made to establish its purity or to determine the magnitude of the corrections to be made.

(3) *Temperature.*—The temperature of the combustion should not be allowed to exceed low redness. At very high temperatures there would be danger of decomposing the ammonia.

(4) *Aspiration of Air.*—Before aspirating a current of air through the tube to remove the last traces of ammonia, the gas under the furnace should be turned out and the tube allowed to cool below redness.

Ruffle Soda-Lime Method.—Many attempts have been made to adapt the soda-lime methods to the determination of nitric nitrogen. Of these, the process devised by Ruffle is the only one that has proved successful.¹ The method is founded on the action of sulfurous vapors on the nitrogen oxides produced during the combustion, whereby sulfuric acid is formed and the nascent nitrogen is joined with hydrogen to form ammonia. By this process all the nitrogen contained in the sample, even if in the nitric form, is finally obtained as ammonia. In the original method the reagents employed were sodium thiosulfate, soda-lime, charcoal, sulfur, and granulated soda-lime. Subsequently, the official chemists substituted sugar for the charcoal.² The method was used for a long time by the official chemists and came into general favor until displaced by the simpler and cheaper processes of the moist combustion method adapted to nitric nitrogen. As finally modified and used by the official chemists, the process is conducted as follows.³

Reagents and Apparatus.—(1) *Standard solutions and indicator.*—Same as in the Kjeldahl method.

(2) *Mixture of fine-slaked lime and finely powdered sodium thiosulfate.*—Equal parts by weight of each dried at 100° C.

(3) *Mixture of finely powdered granulated sugar and flowers of sulfur.*—Equal parts by weight of each.

¹ *J. Chem. Soc.*, **39**, 87 (1881).

² *U. S. Dept. Agr. Div. Chem. Bull.* **16**, 51 (1887).

³ *Ibid.*, **46**, rev. ed., 19 (1899).

- (4) *Granulated soda-lime*.—Same as described under the soda-lime method.
- (5) *Combustion tubes*.—Hard Bohemian glass, 70 cm. long and 1.3 cm. in diameter.
- (6) *U-tubes*.—Large-bulbed U-tubes with glass stopcock, or Will's tubes with four bulbs.

Manipulation.—Clean the U-tube and introduce 10 cc. of standard acid. Fill the tube as follows: (1) Place a loosely fitting plug of asbestos, which has been recently ignited, in the end of the tube to be attached to the absorption apparatus, and add 2.5-3.5 cm. in depth of the thiosulfate mixture. (2) Mix intimately the portion of the substance to be analyzed with 5-10 grams of the sugar and sulfur mixture. (3) Pour on a piece of glazed paper or in a porcelain mortar a sufficient quantity of thiosulfate mixture to fill a depth of about 25 cm. of the tube, add the material as previously prepared, mix carefully, and pour into the tube; shake down the contents of the tube; clean the paper or mortar with a small quantity of the thiosulfate mixture and pour into the tube; and fill up with soda-lime to within 5 cm. of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube and close with a cork. (5) Hold the tube in a horizontal position and tap on the table until there is a gas-channel along the top of the tube. (6) Make connection with the U-tube containing the acid and aspirate, taking care that the apparatus is tight.

Combustion.—Place the prepared combustion tube in the furnace, letting the ends project, so as not to burn the corks. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off at the rate of two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U-tube begins to recede toward the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker or porcelain dish; add a few drops of the cochineal solution, and titrate.

It is much more satisfactory to adhere to the earlier directions for preparing the mixture of thiosulfate and alkali and to make the mixture with soda-lime and without the previous drying of the sodium salt. Ruffle himself says that the sodium thiosulfate should be dry, but should not be deprived of its water of crystallization. The best method to dry the salt without depriving it of its crystal water is to press it between blotting papers. As is seen from the description the method is essentially a reduction process by the action of a powerful deoxidizer in the presence of an alkali. The crystals of the thiosulfate salt cannot be brought into direct contact with a pure alkali, like soda or potash, without forming at once a wet mass, which would tend to cake and obstruct the tube. The soda-lime, therefore, is a mechanical device to prevent this fusion. Where many analyses are to be made, an iron tube, for economical reasons, may be

substituted for the glass, but the glass tube permits a clearer observation. If charcoal is used it should be previously boiled with caustic soda or potash solution, dried, powdered, and preserved in well-stoppered bottles. Although pure sugar is practically free of nitrogen, it is advisable to make a blank determination occasionally and thus ascertain the correction to be made for possible contamination.

MOIST COMBUSTION PROCESS

As long ago as 1868 Wanklyn¹ proposed to conduct the combustion of organic bodies in a wet way, using potassium permanganate as the oxidizing body. About 10 years after this he attempted to extend the method so as to estimate the quantity of proteid nitrogen in a sample by treatment with an alkaline solution in presence of the permanganate salt. It is needless to state that the process of Wanklyn proved to be of no practical use whatever, since it acted differently on different albuminoid matters, and even on the same substance. No other attempt was made to perfect the moist combustion process until Kjeldahl² introduced the sulfuric acid method in 1883. The simplicity, economy, and adaptability of this method brought it into general use. At first the process was applied only to organic nitrogenous compounds in the absence of nitrates, but the modifications proposed by Asboth, Jodlbauer, and Scovell extended its use to all materials, with the possible exception of a few alkaloidal and allied bodies, and it is now generally employed by chemists in all countries, not only for fertilizer control, but also for general work.

Kjeldahl Method.—The process originally proposed by Kjeldahl is applicable only to nitrogenous bodies free of nitric nitrogen. The principle of the process is based on the action of concentrated sulfuric acid at the boiling-point in decomposing nitrogenous compounds without producing volatile nitrogen combinations and the subsequent completion of the oxidation by means of potassium permanganate. The original process has been modified by many analysts, but the basic principle has remained unchanged.

Original Procedure.—The substance is placed in a small digestion flask of resistant glass. Liquids that are not decomposed on heating are evaporated in a thin glass dish, which can be ground up and placed in the digestion flask with the desiccated sample. The strongest sulfuric acid is added in sufficient quantity to secure complete decomposition. The acid must be free of ammonia and be so kept as not to absorb ammonia from the atmosphere of the laboratory. To guard against

¹ *J. Chem. Soc.*, **21**, 161 (1868).

² *Z. anal. Chem.*, **22**, 366 (1883).

danger of error from such an impurity, frequent control determinations should be made, 1 or 2 grams of pure sugar being used as the organic matter. If the acid used contains traces of ammonia, the necessary corrections should be made in each analysis.

After the flask is charged, it is placed on a wire gauze over a small flame. The organic matter becomes black and tar-like, and soon there is a rapid decomposition, attended by the evolution of gaseous products, among which sulfur dioxide is found. Particles of the carbonized organic matter left on the sides of the flask by the foaming of the mass are gradually dissolved by the vapors of the boiling acid as the digestion proceeds. The action of the sulfuric acid is not entirely finished when gases cease to be given off, but the digestion should be continued until the liquid in the flask is clear and colorless, or nearly so. Usually about 2 hours is required to secure this result. For albuminoid bodies it is hardly necessary to continue the combustion until all carbonaceous matter is destroyed. The full complement of ammonia is usually obtained after an hour's combustion, even if the liquid is still black or brown, but with other nitrogenous bodies the case is different, so that upon the whole it is safest to secure complete decoloration.

The temperature must be maintained at the boiling-point of the acid or near thereto, since at a lower temperature the formation of ammonia is incomplete. Since all organic substances are dissolved by the boiling acid, the pulverization of the material need be carried only far enough to secure a fair sample. Many substances, urca, asparagin, and the glutens, for instance, give up practically all their nitrogen as ammonium sulfate when heated with sulfuric acid. In most of the other organic bodies, likewise, fully 90 per cent of the nitrogen is secured as the ammonium salt. In the aromatic compounds, or even in the form of amide in aniline salts, the nitrogen is more resistant to the action of sulfuric acid. In the alkaloids, where the nitrogen is probably a component of the cyclic skeleton, the formation of ammonia is very incomplete. But even in the cases where the conversion of the nitrogen into ammonia is practically perfect, Kjeldahl found it advisable to finish the process by completing the oxidation with potassium permanganate. The permanganate in a dry powdered form is added little by little to the hot contents of the digestion flask, the latter being held in an upright position and removed meanwhile from the lamp. When carefully performed there is no danger of loss of ammonia, although the oxidation is at times so vigorous as to be attended with evolution of light. The permanganate must always be added in excess until a permanent green color is produced. The flask is then gently heated for 5-10 minutes over a small flame. If the heating is too vigorous, a strong evolution of oxygen will take place, with reduction of the manganese compound, the liquid again becomes clear, and there is a loss of ammonia.

After cooling, the contents of the flask are diluted with water, the green color giving place to a brown, with a rise of temperature. After cooling a second time, the mixture is transferred to a distillation flask of about three-quarters of a liter capacity and attached to a condenser which ends in a vessel containing standard sulfuric acid. To prevent bumping, some zinc dust is added to secure an evolution of hydrogen during the progress of the distillation. About 40 cc. of sodium hydroxide solution of 1.3 specific gravity is added, and the stopper is inserted at once to prevent any loss of ammonia. In this case the bumping is prevented until near the

end of the operation, when it begins anew, probably by reason of the separation of solid sodium sulfate. After the distillation the excess of acid remaining in the receiver is determined by a standard alkali solution, and thus the quantity of ammonia obtained is easily calculated.

Kjeldahl preferred to titrate the solution after adding potassium iodate and iodide, a mixture which in the presence of a strong acid sets free a quantity of iodine equivalent to the free acid present. The iodine is then titrated by a standard solution of sodium thiosulfate, starch being used as an indicator. The merits of this method are the sharpness of the end reaction and the possibility of using only a small quantity of the nitrogenous body for the combustion.

Theory of the Reactions.—As is apparent from the preceding discussion, the final product of heating a nitrogenous organic compound with sulfuric acid and an oxidizing body is ammonium sulfate. The various steps by which it is obtained have been traced by Dafert.¹

- (1) The sulfuric acid abstracts from the organic matter the elements of water.
- (2) The sulfur dioxide produced by the action of the residual carbon on sulfuric acid exercises a reducing effect on the nitrogenous bodies present.
- (3) From the nitrogenous bodies produced by the above reduction ammonia is formed by the action of an oxidizing body.
- (4) The ammonia formed is at once fixed by the acid as ammonium sulfate.

According to the theory of Asboth,² the hydrogen that is formed during the action of sulfuric acid on organic matter, when in a nascent state, also aids greatly in the production of ammonia. This idea is based on the fact that with those bodies which afford a deficit of hydrogen the formation of ammonia is imperfect.

Modifications of the Kjeldahl Process.—The moist combustion process has undergone many changes since the first papers of its author were published. They shorten the time of digestion, increase the accuracy, or widen the scope of the materials to which it may be applied. These changes may be divided into three classes as follows:

- (1) Those changes that refer solely to the quantities of substance used for analysis, to the composition of the acid mixture, to the duration of the digestion, to the form and size of the flasks for digestion and distillation, and to the manner of distillation and of titration. Instead of titrating by means of separated iodine, most chemists titrate the excess of acid by a standard solution of an alkali. Ammonium, barium, sodium, and potassium hydroxides are the alkaline solutions usually employed. This method permits the use of a larger quantity of the sample

¹ *Z. anal. Chem.*, **24**, 455 (1885).

² *Chem. Zentr.*, **105** (1886).

and of a larger quantity of acid in the receiver; it also implies the use of a larger digestion flask. In fact, it is now the custom to make the digestion in a special glass flask large enough to be used also for the distillation. This saves one transfer of the material with the possible danger of loss.

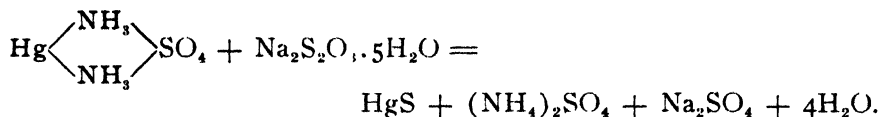
(2) Those changes that involve the introduction of a substance during the digestion for the purpose of accelerating the oxidation. In the original process the only aid to oxidation was the potassium permanganate applied at the end of the digestion. In some of the modifications now under consideration a metallic oxide or metal is applied at the beginning of the digestion. Copper or mercury are the metals usually employed. This modification, known as the process of Wilfarth, will be discussed in a separate paragraph. In another modification, potassium sulfate or sodium sulfate is added to increase the temperature of the digestion and accelerate the process. This will be discussed under the Gunning method.

(3) Those changes, which are even more radical in nature, that have for their object the adaptation of the moist combustion method to oxidized nitrogen (nitrates). The chief feature of this class of changes is the introduction of an organic substance easily capable of forming nitro compounds, for the purpose of holding the oxides of nitrogen and helping finally to reduce them to ammonia. The principal changes were proposed by Asboth, Jodlbauer, and Scovell; they will also be discussed in separate paragraphs.

*Method of Wilfarth.*¹—The basis of this modification rests on the fact that certain metals have the power of carrying oxygen and thus assisting in a catalytic way in the combustion of organic matter. Copper and mercury are best adapted for this purpose, and experience has shown that mercuric oxide or metallic mercury gives the best results. The sample is heated with sulfuric acid. To this is added about 0.7 gram of mercuric oxide prepared in the wet way from a mercury salt free of nitrogen. From 0.1 to 0.3 gram of copper sulfate may be used in addition to the mercury or in place of it. The digestion takes place in the usual Kjeldahl flask. If the boiling is continued until the liquid is entirely colorless, final oxidation with potassium permanganate is unnecessary. If mercury is used, a sufficient quantity of potassium sulfide or sodium thiosulfate is added before distillation to precipitate all the mercury as sulfide and thus prevent the formation of mercurammonium compounds which would produce a deficit of ammonia. The reaction that takes place when sodium

¹ *Chem. Centr.*, 1885, 113.

thiosulfate is used to precipitate the mercury is represented by the following formula :



A convenient strength of the sulfide solution is obtained by dissolving 40 grams of potassium sulfide in 1 liter of water. If copper is used instead of mercury, the addition of potassium sulfide is unnecessary.

When a large excess of potassium sulfide is used, an evolution of hydrogen sulfide occurs, but its presence does not influence the accuracy of the results. The presence of mercuric sulfide in the solution helps to prevent bumping during the distillation, nevertheless it is advisable to use a little zinc.

Paul and Berry¹ found that there may be a loss of 2-25 per cent of ammonia when mercury is used during digestion if the mercury is not precipitated by sulfide or thiosulfate before the distillation. Copper does not cause a loss in this way, and the use of sulfide or thiosulfate is not necessary when copper is used without mercury.

Gunning Moist Combustion Process.—The modification proposed by Gunning² is based upon the observation that in the ordinary Kjeldahl process the excess of sulfur trioxide in the beginning of the operation soon escapes. During the progress of the combustion the acid diminishes in strength until it is below the concentration represented by the formula H_2SO_4 , and in this diluted condition the oxidation takes place more slowly. Gunning proposes to avoid this difficulty by mixing potassium sulfate with the sulfuric acid. This salt, with the sulfuric acid, forms acid salts, which, when heated, lose water more readily than does acid, and, as is well known, act as decomposing oxidizing media even in a higher degree than sulfuric acid, resembling the action of sulfuric acid at high temperatures when under pressure.

By heating this mixture of sulfuric acid and potassium sulfate with organic matters in an open vessel, the water originally present, and also that which is formed during the oxidation, is driven off without loss of acid. For this reason instead of the oxidizing mixture becoming weaker, the acid becomes stronger, the boiling-point rises and this, combined with

¹ *J. Assoc. Official Agr. Chem.*, **5**, 108 (1921).

² *Z. anal. Chem.*, **28**, 188 (1889).

the fluidity of the mass, favors the decomposition and oxidation of the organic matter in a constantly increasing amount.

The mixture used by Gunning consists of one part of potassium sulfate and two parts of strong sulfuric acid. The substances are united by heat, and when cooled are in a semi-solid state; they melt easily, however, on the application of heat and assume a condition that permits pouring from vessel to vessel. The quantity of the sample should vary in proportion to its nitrogenous content from half a gram to a gram. The combustion takes place in flasks similar to those used in the ordinary Kjeldahl process. In the case of liquids, they should be previously evaporated to dryness before the addition of the oxidizing mixture. At the beginning of the combustion there is a violent foaming, attended with evolution of some acid and much water, and afterwards of stronger acid. This loss of acid should not be allowed to go far enough to produce too great concentration of the material in the flask. As soon as the foaming ceases the flame should be so regulated that the volatilized acid will condense upon the sides of the flask. In the end a colorless mass is obtained in which no metals are present, and this mass can be diluted at once with water, treated with alkali, and distilled. According to the nature of the substance, from 30-90 minutes is required for the complete combustion.

Reactions of the Gunning Process.—The various reactions that take place during the combustion according to the Gunning method have been tabulated by Van Slyke.¹

The first reaction to take place is the union of sulfuric acid and potassium sulfate to form potassium acid sulfate in accordance with the following equation: (1) $K_2SO_4 + H_2SO_4 = 2KHSO_4$. When heated the potassium acid sulfate decomposes forming potassium disulfate and water, thus: (2) $2KHSO_4 = K_2S_2O_7 + H_2O$. The potassium disulfate decomposes at a higher temperature, forming normal potassium sulfate and sulfur trioxide, thus: (3) $K_2S_2O_7 = K_2SO_4 + SO_3$. At a sufficiently high temperature the two preceding reactions may take place in one, thus: $2KHSO_4 = K_2SO_4 + H_2O + SO_3$. At the temperature at which these reactions take place, the water that is set free does not recombine with the sulfur trioxide nor with the sulfuric acid that is present in excess, but it is expelled from the mixture; hence the mixture becomes more concentrated during the digestion. The sulfur trioxide set free acts upon

¹ U. S. Dept. Agr. Chem. Bull. 68 (1892).

the organic matter in the powerful manner peculiar to it, and the potassium sulfate, formed in the last reaction, unites with another molecule of sulfuric acid, and the same round of reactions is repeated continuously so long as there is an excess of free sulfuric acid present in the mixture. As the liquid becomes more concentrated with the continuation of the digestion, the boiling-point rises so that the effect is the same as heating under pressure. The danger of too great concentration and risk of con-

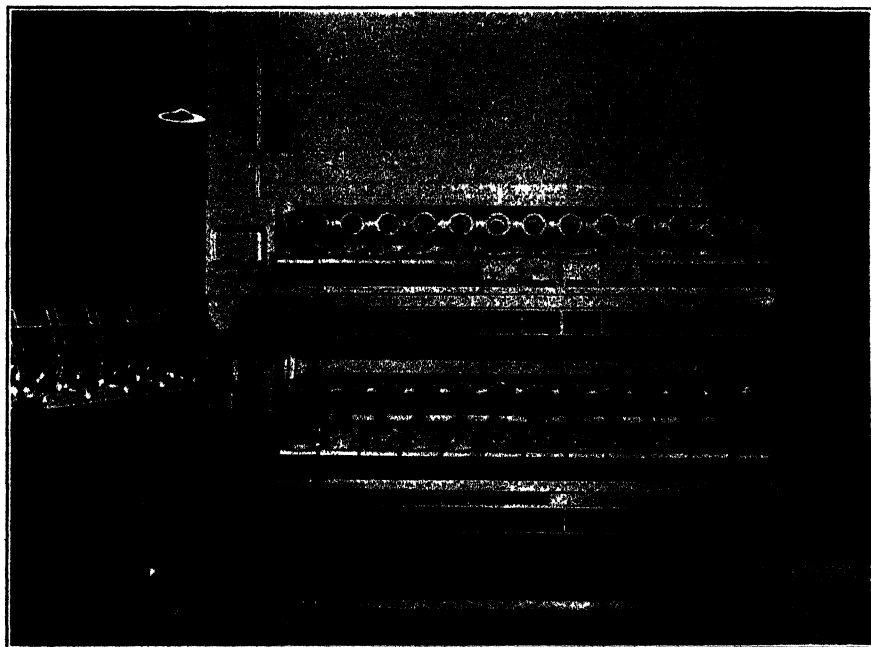


Fig. 1.—Modern Digestion Apparatus for Nitrogen Determinations.

sequent loss of nitrogen is avoided by using larger proportions of sulfuric acid.

As compared with the Kjeldahl, the Gunning method presents the following advantages:

(1) The Gunning method requires fewer reagents. As no form of mercury is used, no potassium sulfide is needed, and there is no risk of loss from the presence of mercurammonium compounds.

(2) The solution to which caustic soda is added is clear, therefore in neutralizing it is an easy matter to avoid great excess of alkali, and in most cases to avoid foaming and bumping in distillation.

Development of the Moist Combustion Process in the A.O.A.C.—The chief changes in the Kjeldahl method, which as printed in 1889 required



FIG. 2.—Modern Distillation and Accessory Equipment for Nitrogen Determinations.

the use of mercuric oxide, consist in the optional use of copper sulfate in place of mercury (1908); the discontinuance of the use of potassium permanganate (1917); and the optional use of sodium thiosulfate to precipitate mercury in place of potassium sulfide (1924).

The use of salicylic acid to adapt the Kjeldahl method for use in the presence of nitrates was proposed by M. A. Scovell in 1887 and studied by him, as reporter, in 1889. The chief change in this method since 1889 consists in the optional reduction with sodium thiosulfate instead of zinc dust, recommended by William Frear in 1891.

The Gunning method was recommended by Frear in 1891; studied by L. L. Van Slyke, reporter, in 1892; and adopted in 1892. The Gunning

method modified for nitrates was studied by C. L. Parsons, reporter, in 1893 and adopted that year. The method that uses both potassium sulfate and mercury was adopted in 1915, but for some reason it was not printed in the methods at that time. It was later adopted under the name of the Kjeldahl-Arnold-Gunning method.

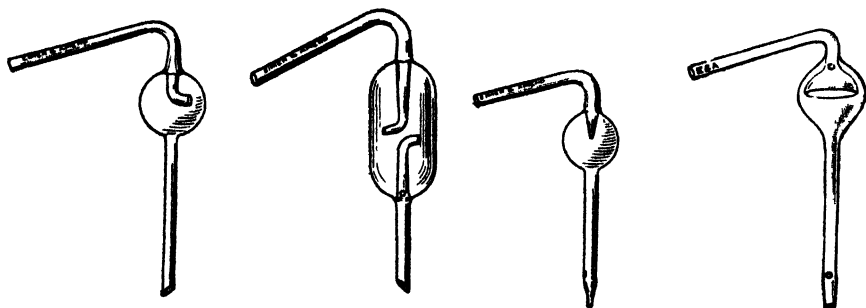


Fig. 3.—Nitrogen Distillation Bulbs.

Official Kjeldahl Method (not applicable in the presence of nitrates).—In order to determine if the sample contains nitric acid or nitrates, apply the following test:

Mix 5 grams of the fertilizer with 25 cc. of hot water and filter. To a portion of this solution add two volumes of concentrated sulfuric acid, free from nitric acid and oxides of nitrogen, and allow the mixture to cool. Add a few drops of concentrated solution of ferrous sulfate cautiously, so that the fluids do not mix. If nitrates are present, the junction shows at first a purple, afterwards a brown color, or if only a very minute quantity is present, a reddish color. To another portion of the solution add 1 cc. of dilute solution of nitrate of soda (3 grams to 300 cc.) and test as before to determine whether sufficient sulfuric acid was added in the first test. The method was published in both the 1920 and 1925 editions of *Methods of Analysis, A. O. A. C.*

The use of mercuric oxide in distillation greatly shortens the time necessary for digestion. The potassium sulfide removes all the mercury from the solution and so prevents the formation of mercurammonium compounds, which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present and that might otherwise escape notice.

Official Gunning Method.—This method is published in all editions of *Methods of Analysis, A. O. A. C.* In distilling, the use of zinc or of some substance to prevent bumping or foaming is generally necessary. The amount of sulfuric acid recommended by Gunning is 2 grams for each gram of potassium sulfate; but Van Slyke found that this mixture is so viscous as frequently to cause troublesome foaming, and that after cooling it cakes in a hard mass, which may be difficult to redissolve. To avoid foaming and caking, he found it effective to increase the quantity of sulfuric acid and to use 3 or 4 grams of acid to 1 of potassium sulfate instead of 2 grams to 1 of potassium sulfate. It is therefore suggested that from 15 to 25 cc. (ordinarily about 20 cc.) of sulfuric acid be used for 10 grams of potassium sulfate. In case the potassium sulfate is not free from nitrogen compounds, one or two recrystallizations will make it pure.

Kjeldahl Digestion Apparatus.—In the Kjeldahl method the digestion of the sample with sulfuric acid is usually conducted in special pear-shaped flasks called Kjeldahl flasks, which are made of resistant glass such as Pyrex or Jena. If the material is to be transferred to another flask for distillation, the capacity is about 250 cc., while if the distillation is to be made from the same flask, the capacity is 500 or 800 cc.

The digestion with acid is usually made with the flasks in an inclined position, with their necks connected with a tube to carry off the fumes, which are very irritating. The tube may be made of lead, be about 5 inches in diameter, have openings about $4\frac{1}{2}$ inches apart and be just large enough to receive the necks of the flasks; it is connected with a flue by means of another lead tube. A Duriron tube especially made for the purpose, with nipples to receive the flasks, may be used.

The draft may be natural, but a forced draft by means of a flame, air jet, steam jet, or fan, is preferable. If a fan that comes in direct contact with the fumes is used, it should be made of lead, Duriron or some other resistant metal or alloy. An iron pipe anywhere in the system may soon be closed completely with sulfate of iron. The use of a good fan renders the use of a hood unnecessary. Provision should be made to collect the acid that condenses.

The digestion flasks may be heated by gas or electricity. Gas of a proper quality is easily adjusted and regulated. A good arrangement consists of six or more gas burners, each set on a gas cock in an iron pipe. The distance between the burners should depend on the distance between

the centers of the hole or nipples in the fume pipe that receives the digestion flasks. These burners can easily be replaced.

Discussion of Details.—*Precautions Necessary during Digestion.*—If the digestion flask is exposed to the flame above the acid during digestion, loss of ammonia may result, especially when a short flask is used or the contents of the flask are boiled to a small volume. When the contents of the flask were boiled to a volume of about 5 cc., Paul and Berry found losses of 13-18 per cent of the nitrogen when potassium sulfate was not used, and 2.5-4 per cent when it was used. Losses are prevented if the volume of the liquid is left well above 10 cc. Asbestos guards may be used to prevent the flame from touching the glass above the liquid. They consist of a sheet of asbestos about $\frac{1}{4}$ inch thick, with holes of such size that only the part of the flask below the liquid is exposed to the flame. Hibbard¹ decided that the loss when the acid was boiled too low was caused by driving off too much acid and not by the flame heating the flask above the level of the acid.

When protein substances are heated too rapidly at the beginning of the digestion, particularly when acid has not come in contact with all of the sample, low results are obtained owing to the loss of nitrogen in volatile forms, possibly by charring of particles by the heat. In order to overcome this loss, the acid should be mixed with the sample and the sample should be digested slowly and carefully at first. This period, or that required for the expulsion of water when aqueous solutions are under examination, should not be considered as part of the time required for digestion. Only the time of actual boiling of the sulfuric acid should be counted. Decolorization of the mixtures is not a safe indication of complete hydrolysis. In some cases, as with pyridin derivatives, the digestion mixture may be colorless, even though little or no hydrolysis to ammonium sulfate has taken place; while in other cases, as when an excess of carbohydrates is present, the mixture may still be discolored after all the nitrogen has been converted to ammonium sulfate.

Special Rubber Stoppers for Kjeldahl Distillation.—Under the hard usage required by the Kjeldahl method, the angle of the ordinary rubber stoppers becomes greater, the stopper is harder to fit, and work is lost or the stoppers require frequent replacement. The special rubber stoppers devised by the Bureau of Chemistry and Soils of the United States Department of Agriculture are more durable; they also have a less acute angle and so fit the flask better. The stoppers for 500 cc. flasks are 31

¹ *Ind. Eng. Chem.*, **2**, 463 (1910).

mm. at the large end, 28 mm. at the small end, and 31 mm. long with a 9 mm. hole. The stoppers for 800 cc. flasks are 31 mm. at the small end, 34 mm. at the large end, and 31 mm. long with a 10 mm. hole.

Measuring Reagents.—The mercuric oxide or powdered copper sulfate may be added by means of a small spoon holding approximately 10 grams; pellets containing 0.7 gram of mercuric oxide may now be purchased. Mercury may be measured by means of a spoon, or in a mercury measuring apparatus. An apparatus for metallic mercury can be made from a separatory funnel that has a stopcock with a hole of suitable size by stopping the hole in the stopcock with litharge and glycerol or other cement, and then making a hole of the required size on one side or on both sides of the stopcock. Mercury is delivered by turning the stopper. A similar apparatus may be made of metal.

Kjeldahl Distillation Apparatus.—The Kjeldahl distillation apparatus consists essentially of a block-tin tube in a tank or tub cooled by water, with a scrubber-bulb tube at the upper end to prevent alkali spray from going over, and a bulb tube at the lower or receiving end to prevent the acid in the receiver from being sucked back far enough to come in contact with the tin tube.

The connecting bulbs and the condensers are made in a variety of forms. The condensers are usually arranged in sets of six or more. The tin tubes may be run through copper tanks, six or more to a tank, or they may run singly through iron pipes so arranged that water can be run through them singly or in groups. The end of the bulb tube should dip into the acid, diluted to about 100 cc., and the distillate should have a lower temperature than the acid, otherwise it may rise to the surface of the acid and cause loss of ammonia. This has actually been observed. Beakers, flasks or even milk bottles or fruit jars, may be used as receivers for the distillate.

It is usually well to color the acid with the indicator to be used; then a change in color will indicate too little acid, and additional quantities can be added if necessary. If the quantity of acid is not sufficient to neutralize all the ammonia, the results are frequently inaccurate.

Use of Zinc in the Distillation.—The use of a small amount of granulated zinc (20 or 40 mesh) during the distillation is always advisable to prevent bumping, which sometimes occurs with such explosive violence as to blow the stopper out of the Kjeldahl flask and spray hot caustic soda solution over the room and on the clothing or even into the eyes of the analyst.

The use of an excess of zinc, however, should be avoided as it may result in the distillation of some mercury into the condenser. This will injure block tin coils, though it may not affect the analysis.

Copper Distilling Flasks.—To avoid the expense and annoyance attending the breaking of the distilling flasks, Patrick¹ proposed to make them of copper. A half-liter size, as made for the evolution of oxygen for experimental purposes, may be used. A little excess of potassium sulfide is used to make up for that which might be consumed by the copper. About 25 cc. of this solution is recommended. No zinc or pumice stone is required to prevent bumping, and the distillation may be finished within 30 minutes. A slight corrosion of the flasks may be caused by the sulfide employed, but if the Gunning oxidation process is practised, this danger would be avoided.

Quantity to Distil.—The official method states that 150 cc. of the distillate will generally contain all the ammonia. Hibbard experimented with different quantities of distillate and found that 75 cc. contained nearly all the ammonia. Paul and Berry, making similar experiments, found that practically all the ammonia was distilled over with the first 75 cc. of the distillate, and all of it with 100 cc. The requirement of 150 cc. thus appears ample.

Titration of the Solution.—A good light (preferably daylight) is necessary during the titration. An electric light under semi-transparent opal glass set in the titration table may be found satisfactory. The change in color is most readily detected when the solution to be titrated is placed next a similar solution already titrated to slight alkalinity. When many titrations are to be made, time is saved by using an overflow buret connected to a reservoir from which the buret can be filled either by gravity or by air pressure. The former method is probably more convenient.

Calculation of Results.—Calculation is simplified and the work reduced by proper use of normal weights. If 0.2 *N* alkali is used, 1 cc. is equal to 0.0028 gram of nitrogen. If 1.4 grams of substance is weighed out, 1 cc. of the standard alkali equals $\frac{0.0028}{1.4} \times 100 = 0.2$ per cent of nitrogen.

The calculation may be further simplified and the work reduced by using a fixed pipet and a buret graduated to show the quantity contained in it instead of the quantity delivered. With 0.5 *N* acid and 0.2 *N* alkali, there could be used a fixed overflow pipet delivering 20 cc. and a 50 cc. over-

¹ U. S. Dept. Agr. Div. Chem. Bull., **31**, 142 (1897).

flow buret graduated as described. Both should be connected to reservoirs to permit rapid filling. For the analysis 1.4 grams of substance is used, and the ammonia is distilled into 20 cc. of 0.5 *N* sulfuric acid. The titration then takes place as usual. The reading of the buret $\times 0.2$ equals the percentage of nitrogen in the fertilizer. The use of a fixed quantity of acid and a buret graduated to show the quantity of alkali in it saves calculation and corresponding errors. It requires larger quantities of standard acid and alkali, since the amount of acid in the receiver cannot be adjusted to the nitrogen in the substance under analysis.

In some laboratories, 1 gram of substance, or a similar even weight is used and the result either read from a table, or a special solution is used so that 1 cc. equals an even percentage of nitrogen. In laboratories where the acid and alkali are used for other work in addition to the estimation of nitrogen, it is generally more convenient to prepare the solutions on a normal basis and to use a factor weight.

Use of Permanganate of Potash Discontinued.—Kjeldahl used finely powdered permanganate of potash to complete the oxidation of the organic material. L. L. Van Slyke,¹ referee in 1892, found that with the Kjeldahl method permanganate was not needed with bone meal, but that it produced nearly 0.10 per cent more nitrogen from cottonseed meal. With the Gunning method he found the use of permanganate of potash unnecessary. Losses of nitrogen due to the use of permanganate in the Kjeldahl method were studied by Frear, Thomas and Edisten.² Determinations were made by two analysts on several fertilizer samples, with and without nitrates, by varying the quantity of permanganate added and the manner and time in relation to completion of the heating process. It was shown by the results obtained that the loss depends somewhat upon the quantity of permanganate, but chiefly upon the time of addition and that it might be as much as 0.83 per cent. If the addition was delayed for 2 minutes after the mixture was removed from the flame, no loss was observed. This implies that there is a critical temperature below which the reaction causing the loss does not take place.

Kjeldahl states that when permanganate is added the reaction is vigorous enough to cause evolution of light, and that no case of the appearance of luminosity was noted when permanganate was added the instant the mixture was removed from the flame. This phenomenon occurred chiefly from 4-12 minutes after removal from the flame. Kjeldahl's mention of

¹ U. S. Dept. Agr. Bur. Chem. Bull. **35**, 71.

² *J. Assoc. Official Agr. Chem.*, **3**, 221 (1919).

the occurrence of luminosity suggests that the addition of permanganate must have been delayed longer than was indicated by the adverb "immediately."

The use of permanganate of potash was also studied by Referee Daudt.¹ Its use was discontinued in 1917 following the recommendation of Referee Phelps.² It should be observed, however, that the experiments of Phelps were made with the mercury-potassium sulfate method, not with mercury and sulfuric acid alone.

Sodium Thiosulfate to Precipitate Mercury.—The use of sodium thiosulfate in place of potassium sulfide was recommended by Neuberg³ in 1902. Daudt, the associate referee in 1917, reported that the quantity necessary for complete precipitation of 0.7 gram of mercury (as sulfide) is 1 gram and that the manner of adding the reagent has no influence on the results.

A. L. Prince,⁴ the associate referee in 1924, reported that the use of sodium thiosulfate as a precipitant for mercury in the Kjeldahl method appeared to be quite satisfactory and that its use should be left to the discretion of the analyst. The optional use of sodium thiosulfate was adopted in 1924.⁵

Use of Sodium Sulfate.—Sodium sulfate was used in place of potassium sulfate in the Gunning method during the war, owing to the high price of potash salts. Its use was adopted officially in 1917⁶ after work had been done by a number of collaborators and referees. Review of the literature indicates that while sodium sulfate is satisfactory, potassium sulfate is on the whole more effective and is more likely to give maximum results in a shorter time.

Quantity of Potassium or Sodium Sulfate.—The relative quantities of sulfuric acid to potassium or sodium sulfate influences the rapidity and completeness of the hydrolysis. An excess of sulfuric acid increases the length of time required for complete decomposition of the material, or produces low results owing to incomplete decomposition. This may explain the variations in duplicate analyses or in different laboratories on the same sample. Phelps and Daudt,⁷ using lead condensers, found for

¹ *J. Assoc. Official Agr. Chem.*, **4**, 366 (1921).

² *Ibid.*, 241.

³ *Beitr. Chem. Physiol. Path.*, **2**, 214 (1902).

⁴ *J. Assoc. Official Agr. Chem.*, **8**, 410 (1925).

⁵ *Ibid.*, 263.

⁶ *Ibid.*, **4**, 241 (1920).

⁷ *Ibid.*, **3**, 218 (1919).

example that when 25 cc. of acid and 10 grams of potassium sulfate were used with mercury, incomplete decomposition was obtained, but that when 15 cc. of sulfuric acid was used with from 10 to 30 grams of potassium sulfate excellent results were secured.

Use of Copper.—Copper, in the form of copper sulfate, was recommended by C. L. Penny in 1907, and the use of 0.1-0.3 gram of copper sulfate in addition to mercury or in place of it was adopted in 1908.¹ According to Paul and Berry,² mercury with potassium sulfate is much more effective in reducing the time of digestion than copper; while copper may be used, the time of digestion must be longer. Thus, while the maximum amount of protein in flour was obtained by digesting with mercury 1 hour after the acid was cleared, it required 3 hours for copper; with powdered milk, $\frac{1}{2}$ hour for mercury, 3 hours for copper; with gelatin, 2 hours for mercury, 6 hours for copper; with egg albumin, 1 hour for mercury, 5 hours for copper; with tarrage 3 hours for mercury, 7 hours for copper. This is the time of digestion after the liquid is clear, not the total time of digestion. Quantities of copper sulfate varying from 0.1 to 1.0 gram made little difference.

Jensen³ found copper or mercury (with potassium sulfate) equally effective with the substances he studied, except with dried blood; in this case, $1\frac{1}{2}$ hours was sufficient for mercury, but 3 hours was required for copper.

Phelps and Daudt⁴ reported on the use of copper in 1916. The results they obtained with the method when they used potassium sulfate with copper sulfate in lieu of oxide of mercury, were very satisfactory. The oxide of mercury seemed to be a little more effective and rapid in its catalytic action than copper sulfate. Perhaps the digestion in the case of copper should have been more prolonged than with mercury, as was indicated by the work of one of the collaborators. Some results on time of digestion with potassium sulfate and mercury, obtained when dried blood was used, indicated that the maximum nitrogen was reached in 2 hours, though there was an increase of only 0.03 per cent over the result obtained in 1 hour digestion.

Indicators Used.—Cochineal was the indicator specified in the official method until 1916, when the Committee on Revision of Methods put in

¹ U. S. Dept. Agr. Div. Chem. Bull. **122**, 183.

² J. Assoc. Official Agr. Chem., **5**, 108 (1921).

³ J. Ind. Chem., **7**, 38 (1915).

⁴ J. Assoc. Official Agr. Chem., **3**, 214 (1917).

methyl red. Litmus and rosolic acid have been used, but the official analyst should use one of the indicators prescribed in the official methods.

Time of Digestion.—The time of digestion with sulfuric acid depends upon the kind of material and the method used. If sulfuric acid and mercury, or copper, are used, the time required for complete decomposition of the substance may be considerably longer than if sulfuric acid, potassium sulfate (or sodium sulfate) and copper or mercury are used. As already pointed out, the Gunning mercury method is quicker than the Gunning copper method.

T. C. Trescot¹ found the results by the Gunning mercury method when carried out with a 1½ hour period of digestion were higher than those by the Gunning method when the digestion was continued 3-4 hours, excepting in the cases of cheese and flour, when they were practically the same. They were also practically the same as the results of the Kjeldahl method with 3-4 hours' digestion, excepting in the cases of leather, leather waste, linseed meal, and gelatin, in which they were slightly higher. With cyanamide it was found necessary to digest for 2½ hours.

Jensen² found that digestion of 1½ hours was sufficient for the substances studied except blood, when the Gunning-mercury and Gunning-copper methods were used. The Gunning-copper method required 3 hours for dried blood. J. M. Pickel³ studied short periods of digestion and found that 30 minutes of vigorous digestion was sufficient for many fertilizers. However, this short period of digestion is not to be recommended for general work.

Two hours' brisk digestion is sufficient for usual materials, but longer periods will be needed for refractory organic compounds.

Preparation of Standard Solutions.—The acids now used are hydrochloric acid standardized by silver nitrate, or sulfuric acid tested by barium sulfate. In 1889, standard hydrochloric acid was prescribed; it could be standardized by means of silver nitrate, by potassium tetroxalate, by sodium carbonate, or by ammonium chloride, in which case the ammonia was liberated with caustic soda and collected in the acid to be tested. The use of sodium carbonate was discontinued in 1890. The methods of standardization were studied by the referee in 1892.⁴ All methods for standardization except by means of silver nitrate were discontinued in

¹ *J. Ind. Eng. Chem.*, **5**, 914 (1913).

² *Ibid.*, **7**, 38 (1915).

³ *Ibid.*, 357.

⁴ U. S. Dept. Agr. Bur. Chem. Bull. **35**, 75, 80.

1892.¹ The use of standard sulfuric acid was adopted in 1893. Standard ammonia was required until 1894, when it was changed to standard alkali, with ammonia recommended.

The preparation of a standard acid is facilitated by the following method.

Prepare the desired quantity and make two or three preliminary titrations. Adjust the solution so that it is a little stronger than that desired. If the acid is made a little strong in the first adjustment, it may be easily and accurately diluted, but if the analyst is so unfortunate as to make it a little weak, the entire process must be gone over again. The preliminary adjustment is easily made by the following method. Suppose 0.5 *N* sulfuric acid is being made up and titrated with 0.2 *N* caustic soda, and it requires 56.4 cc. of the soda to neutralize 20 cc. of the acid. A titration of 50.5 cc. of 0.2 *N* alkali for 20 cc. of acid is desired for the preliminary preparation of the solution. Then $\frac{56.4}{50.5} = 1.1168$ cc., the volume to dilute 1 cc. If 40 liters of acid has been made up, then $1.1168 \times 40,000 = 44,672$ cc., the volume to dilute 40 liters. The acid is now a little strong and must be diluted accurately after the strength has been determined by precipitation with barium chloride.

After the preliminary adjustment, the strength of the acid is determined by precipitation as barium sulfate, three portions of 10 cc. each being used. Then by means of a calculation similar to that already made, the quantity of water to be added, or of acid to be diluted to a given volume, is easily calculated and the adjustment made.

For example:

10 cc. of 0.5 *N* acid is found to yield 0.5894 gram of barium sulfate.

10 cc. of 0.5 *N* acid should yield 0.5836 gram of barium sulfate

$$\frac{0.5894}{0.5836} \times 40,000 = 40,397 \text{ cc., volume to dilute 40 liters.}$$

The same method of procedure can be used for making up any standard solution.

Care of Standard Solutions.—Standard solutions are liable to change and should be tested frequently. If a large quantity is made up, it is well to distribute it in bottles of 2-4 liters capacity, filled nearly full and sealed with paraffin. If burets or pipets are fed from an aspirator by gravity, the solution should be protected by a U-tube containing enough of the standard solution to seal the bend, and it should be replaced frequently. The aspirator should be of moderate size, about 2 liters. In warm climates sulfuric acid and sodium hydroxide are probably preferable to hydrochloric acid and ammonia. Titration of the solutions should be made in the same order as in the analyses, that is the alkali should be run into the acid. Frequent check titrations should be made, and the solutions should

¹ U. S. Dept. Agr. Bur. Chem. Bull., 91.

be adjusted when necessary; if the analyst has not been in the habit of making such checks, he may be surprised at the comparative frequency that such adjustments are required, even when the solutions are carefully protected.

The standard alkali should also be titrated against the acid measured by the buret or pipet used in the regular analytical work, and these should be carefully calibrated. The results should agree with titrations made with the use of other calibrated instruments.

Other Methods of Standardizing the Acids.—The use of standard hydrochloric acid is official. It is made by precipitation as silver chloride, a highly accurate method when properly carried out. The use of potassium tetroxalate was at one time official. Sodium carbonate and sodium bicarbonate are used by some analysts, but they are not official in the A. O. A. C. It is best to follow the official method. Sodium carbonate¹ is prepared by heating sodium bicarbonate (or sodium carbonate) of the highest purity in a platinum vessel to 270° C., until the weight is constant. It is cooled in a desiccator, and a weighed portion (about 1 gram) is dissolved in water and titrated with standard sulfuric acid, methyl orange being used as an indicator. When the solution becomes slightly red it is boiled to remove carbon dioxide, cooled and titrated to the first color change. The results are calculated as usual. Sodium bicarbonate may be prepared from a solution of pure sodium carbonate by precipitation with carbon dioxide gas, filtration, and washing two or three times with cold water.

Use of Boric Acid to Absorb the Ammonia.—The use of boric acid to absorb the ammonia produced in the various modifications of the Kjeldahl method is interesting, but this method is not official. By use of a suitable indicator the ammonia may then be titrated directly. The boric acid reacts neutral to the indicator selected, while the ammonium borate reacts alkaline. The use of boric acid also obviates the need for a standard alkali, since a 4 per cent solution of boric acid is used as the absorbing medium. The boric acid has the disadvantage, however, that it loses ammonia if the temperature of the solution becomes 60° C. or more, and it also requires a blank on the reagents, partly due to dilution with water. When 50 cc. of 4 per cent boric acid is placed in the receiving vessel, no blue color is developed on the addition of bromphenol blue, but when diluted to 200 cc. the blue color immediately develops and requires about

¹ Oil and Fat Industries, May, 1929, p. 29.

0.30 cc. of 14.01 *N* sulfuric acid to cause it to disappear, according to Markley and Hann.¹ A similar effect occurs with methyl orange. A blank of 0.30 cc. acid would be subtracted under the conditions given above. The indicator solution may be made by heating 0.1 gram of bromphenol blue with 3 cc. of 0.05 *N* sodium hydroxide until dissolved and then diluting to 250 cc. with distilled water.

Work of Paul and Berry.²—In a study of various factors which affected the Kjeldahl method or its modifications, Paul and Berry found that when enough acid is used in the receiving flask to neutralize 85.5 per cent of the ammonia distilled over, the quantity of nitrogen recovered was 99.87 and 99.68 per cent. They concluded, therefore, that while it is advisable to use sufficient acid to neutralize all the ammonia to be distilled over, it is not absolutely necessary. However in control work, it is frequently found that results are low when an excess of acid is not used, especially in warm weather. They found that practically all the ammonia was distilled over with the first 75 cc. of the distillate and all of it with 100 cc. If sulfide was not used to precipitate the mercury before distillation, a loss of from 2 to 15 per cent of ammonia resulted when mercury was used during digestion.

When 10 grams of either potassium or sodium sulfate was used, maximum results were reached in 6 hours, but with 5 grams an excessive time was required to clear up the solution and maximum results were not reached in 6 hours' additional digestion. With mercury alone the results were not satisfactory since approximately 10 hours was required to complete the digestion. However, when both mercury and potassium sulfate were used maximum results were obtained with 2 hours' digestion after clearing. There appeared to be little difference between the results when 5 grams or 10 grams of potassium sulfate was used with mercury. When copper sulfate alone was used, maximum results were not reached even after 10 hours' digestion, but with both copper sulfate and potassium sulfate maximum results were reached after 6 hours. Mercury is much more efficient than copper, as when mercury alone was used maximum results were reached in 10 hours, while with copper alone this was not the case. This conclusion is also borne out by the fact that with mercury and potassium sulfate maximum results were obtained in from 2 to 3 hours, while with copper sulfate and potassium sulfate they were reached

¹ *J. Assoc. Official Agr. Chem.*, **8**, 457 (1925).

² *Ibid.*, **5**, 108 (1921).

in 5-6 hours. Then again, a longer time is required to clear up the solution when copper sulfate is used than when mercury is used.

It would appear that potassium sulfate is a little more efficient than sodium sulfate, as with 5 grams of the former the solution was clear in 4 hours, while with 5 grams of sodium sulfate the solution was not entirely clear after 6 hours. The conclusion is drawn that the most efficient combination is mercury and 5-10 grams of either potassium or sodium sulfate. Mercury costs more than copper sulfate, but it requires less time and gas. There is no advantage in the combination of mercury and copper sulfate.

Other results tend to show that from 0.5 to 0.7 gram of mercuric oxide is the proper amount to use. In fact, 0.3 gram gives maximum results with 3 hours' digestion after clear, while 0.5 gram or over gives the maximum in 2 hours. There certainly is nothing to be gained by the use of more than 0.7 gram.

The quantity of copper sulfate used had very little influence on the results. When 0.5, 1, and 2 gram samples were tested, maximum results were reached with a slightly shorter time of digestion with the smaller sample, but great difficulty was experienced in getting concordant results. This is undoubtedly due to the fact that the smaller the sample weighed, the greater the difficulty of obtaining a representative sample, and the chance of slight unavoidable errors. Everything considered, it seems that a 2 gram sample of cottonseed meal and similar substances is preferable to other quantities.

Paul and Berry also found that 1 hour digestion with mercury and 2 hours with copper sulfate is sufficient in the case of flour, $\frac{1}{2}$ hour and 2 hours in the case of powdered milk, 2 and 6 hours for gelatin, 1 and 5 hours in the case of egg albumin, and 4 and 8 hours for tankage. The use of potassium permanganate is unnecessary.

The reagents, in addition to sulfuric acid, which are most economical of time are potassium or sodium sulfate with mercuric oxide and potassium sulfide. Copper sulfate may be used in place of mercuric oxide and potassium sulfide, but the time of digestion must be lengthened. The time of digestion after clearing is of prime importance and should be determined for each substance to be examined; in most instances 3 hours is sufficient. Nitric acid should not be used in a hood in which it is the intention to make nitrogen digestions since nitric fumes may be absorbed by the acid.

Work of Phelps and Daudt.¹—Phelps and Daudt made an extensive study of the Kjeldahl method, using a variety of organic compounds. For the usual materials, excellent results were obtained when the digestion was made for 2½ hours with a boiling mixture of 25 cc. of sulfuric acid, 0.7 gram of mercuric oxide and 10 grams of potassium sulfate. When sodium sulfate was substituted for an equal weight of potassium sulfate the results were below the theory. Return condensers constructed of lead were tested; they served not only to prevent the vaporization of sulfuric acid but to retain the acid ammonium sulfate even when excessive quantities of ammonia sulfate were obtained. Further studies include a number of amines, other organic compounds and special methods for azo and hydrazine compounds, which are discussed later in the chapter. An apparatus for aeration is also described.

The Preferred Method.—Careful study of the literature leads to the conclusion that the shortest and most accurate method for total nitrogen is the method using both mercury and potassium sulfate. All the work of Paul and Berry, of Phelps and Daudt, of Daudt, of Trescot, and of Pickel points unmistakably to this conclusion. The use of copper sulfate in place of mercuric oxide, the omission of potassium sulfate, or the use of sodium sulfate in place of potassium sulfate, while satisfactory perhaps for some easily decomposed materials, usually requires a longer period of digestion to secure the same amount of nitrogen as secured by the mercury-potassium sulfate method. Hence, the mercury-potassium sulfate method is to be preferred, especially to meet the modern requirements of speed and accuracy. The evidence regarding the use of mercury and potassium sulfate in the estimation of total nitrogen in materials containing nitrates is not so clean cut, since some analysts seem to secure better results without their use; nevertheless, it indicates that this method is the better.

Degree of Accuracy Attainable.—The Gunning-Kjeldahl method gives a high degree of accuracy when it is properly used. The American Oil Chemists Society sends out a series of 30 samples of cottonseed meal during the season, one sample a week, the analyses being made with the use of potassium sulfate and mercury. Many of the analysts deviate only a few hundredths of a per cent (of ammonia) from the accepted average.

In 1928² the number of collaborators was 80; the average number of results ± 0.02 per cent was 40; the average number ± 0.05 was 65, and

¹ *J. Assoc. Official Agr. Chem.*, **3**, 218, 306 (1919-20).

² *Oil and Fat Industries*, **5**, 147 (1928).

the average number ± 0.10 was 77 on each sample. While it is true that some of the analysts run six or more tests on each sample, this is not essential, and the accepted average is not necessarily the correct percentage of nitrogen. This work, however, shows the high degree of accuracy possible with the method after the analyst has checked all the details.

Wholesale Nitrogen Determinations.—Systematic arrangement of apparatus and division of work may make possible a large number of nitrogen determinations in a day. According to Roettger,¹ 500 determinations of nitrogen or protein in cottonseed products could be made in a day by three men and the apparatus he describes. While it would not be possible to make so many analyses of fertilizers that contain nitrates owing to the longer period of digestion required, and few laboratories require so many a day, the details are interesting.

The Kjeldahl flasks, in groups of ten, are attached to wooden sticks, about 1 inch square and a little less than 3 feet long, by means of 10 small steel spring clips, which just fit the necks of the flasks. The flasks remain attached to these sticks during the digestion, distillation, and washing. The flasks are supported at the balance table and at the work table by slipping one end of each stick into a square hole which just receives it. Six sticks, or sixty flasks, are thus held at a work table while sodium sulfate and copper sulfate are put in previous to weighing, and the flasks are likewise held near the balance table to receive the samples. The flasks, on a small roller truck, are then run beneath a liter acid buret, from which concentrated acid is introduced. The buret is filled by an iron syphon, with an iron stopcock, from a carboy of acid supported above the buret. The digestion takes place on 80 Gilmer electric heaters set in front and below the lead fume pipe. The large pipe has $\frac{3}{4}$ " x 2" nipples with $\frac{1}{8}$ " holes. These holes are small so that the suction supplied by the exhaust fan will be evenly distributed along the pipe and also make it unnecessary to stopper any openings not in use to secure a good draft on the rest. The stills are perpendicular iron pipes containing block tin condensers, with Gilmer electric heaters. There are three sets of these, each with a capacity for 20 flasks, and they are placed in a line parallel to the digestion apparatus, with only a small aisle between. The ammonia distillate is collected in pint milk bottles, which are handled in racks provided with hinged covers from the time they are washed until set in place beneath the stills. The covers close around the necks of the bottles, leaving the tops open for draining or filling with standard acid and indicator. Suitable racks for these cases are provided under the table, where the standard acid is added, and after being washed they remain upside down in these racks until needed. For charging the milk bottles with the proper quantity of standard acid a double automatic pipet is used. The indicator is added through a syphon and rubber tube with a bead valve from a stock bottle placed on the shelf above. Water is added from a perforated ring of copper pipe that fits just inside

¹ *Cotton Oil Press*, 5, 33 (1921).

the top of the bottle. The final titration is made with a 10 cc. buret, which is filled through a side arm at the bottom. A table giving the percentage of ammonia corresponding to the buret reading is hung near the buret, and printed forms for recording results are used. In the bottom of the sink used for cleaning the Kjeldahl flasks there is a $\frac{3}{4}$ " pipe with a number of perpendicular jets of $\frac{1}{4}$ inch pipe at the proper distance to receive the Kjeldahl flasks. Rubber stoppers are placed near the bottom of these jets to protect the tops of the flasks. The set of flasks is turned upside down, water is turned on and 10 flasks are quickly washed. In the other sink there is a similar arrangement for washing the milk bottles, the jets being so spaced that ten bottles can be washed by merely inverting the rack over the nozzles and turning on the water. Several racks on wheels are used for transporting the sticks with the Kjeldahl flasks from one place to another or storing them when not in use.

The work is divided as follows: One man supplied with prepared and numbered samples can make 500 weighings in the forenoon and titrate in the afternoon. He is furnished with flasks previously charged with the sodium sulfate and copper by a second worker, an assistant who also adds strong sulfuric acid to the flasks after the samples have been weighed, draws the standard acid into the milk bottles, and changes the bottles below the stills as fast as a batch is finished. A third worker stands between the digestion table and stills and conducts those stages of the work. Each group of 20 determinations is handled as a unit, and groups are put on to digest at 20 minute intervals. As 1 hour and 20 minutes is required for digestion, the 80 stoves are loaded and cleared once in that time; at the end of this period the fifth group replaces the first group. Distillation and the changing of bottles, etc., require 1 hour, therefore 60 distillations are on the three batteries of 20 stills each hour. Three digestions on the eighty stoves (240 determinations) require 4 hours; the 60 stills complete 240 distillations in the same time.

CHANGES IN KJELDAHL METHOD TO INCLUDE NITRATES

Modifications of Asboth.¹—In order to adapt the moist combustion process to nitric nitrogen Asboth proposed the use of benzoic acid. For half a gram of saltpeter, 1.75 grams of benzoic acid should be used. The principle on which the use of benzoic acid rests is found in the fact that it easily yields nitro compounds and thus prevents the loss of the nitrogen oxide. The nitro compound can be subsequently converted into ammonia by treatment with sulfuric acid and finally with potassium permanganate.

Variation of Jodlbauer.—The benzoic acid method, although a step forward, is not entirely satisfactory for the estimation of nitrates by moist combustion. Jodlbauer² proposed to substitute phenolsulfuric acid for the benzoic. From 0.2 to 0.5 gram of a nitrate is treated with 20 cc. of con-

¹ *Chem. Centr.*, 1886, 161.

² *Ibid.*, 433.

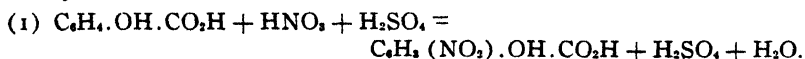
centrated sulfuric and 2.5 cc. of phenolsulfuric acid, together with three grams of zinc dust and five drops of a solution of platinic chloride. If the substances used are very rich in nitrates, it is advisable to rub them first with dry gypsum.

The theory of the process rests on the fact that by a careful admixture of a nitrogenous substance diluted with land plaster and phenolsulfuric acid, it is possible to change the nitric acid into nitrophenol, and by the reducing action of zinc dust to change the nitro-product formed into amido-phenol, which later is transformed into ammonium sulfate by heating with sulfuric acid. At the same time all other nitrogenous compounds present in the substance, as with Kjeldahl's method, form ammonium sulfate, the only difference being that addition of mercury is here absolutely necessary for the complete transformation of the slowly decomposed amido-phenol, and this necessitates the decomposition of the nitrogenous mercury compounds formed in the solution by potassium sulfide, which is added after or with the soda-lye.

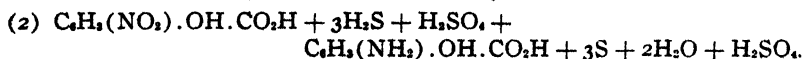
Salicylic Acid Method.—The introduction of the use of salicylic acid as the proper reagent to prevent the loss of nitrogen when a nitrate is acted on by sulfuric acid is due to Scovell.¹ He noticed that the action of phenol was too violent to protect the process from loss of nitrogen. After a careful trial of many organic compounds capable of forming nitro-compounds under these circumstances, salicylic acid was selected as the most promising reagent. Rigid trials by Scovell and other referees of the A. O. A. C. extending over many years confirmed the propriety of this choice. This method has also been found to be accurate in the presence of chlorides as well as of nitrates.

Theory of the Process.—The theory of the process by which salicylic acid converts nitrates to ammonia is as follows:

(1) When salicylic acid and sulfuric acid are added to a nitrate, the sulfuric acid takes up water, and one of the hydrogen elements of the salicylic acid is replaced by NO_2 , forming nitro salicylic acid. This reaction takes place without heat. It is probably mononitro and not dinitro salicylic acid that is formed, and the reaction is probably as follows:

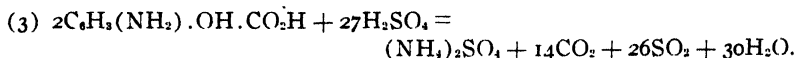


(2) Subsequently when sodium thiosulfate is added the hydrogen sulfide liberated reduces the nitro salicylic acid to amido salicylic acid as follows:



¹ U. S. Dept. Agr. Div. Chem. Bull., 16, 51; 19, 47.

When zinc is used, nascent hydrogen effects the reduction. The strong sulfuric acid and heat on the amido salicylic acid break it up and there is formed ammonium sulfate, carbonic acid, sulfur dioxide and water, as follows:



Similar reactions probably occur when benzoic acid or phenol is used, but either the nitro compounds are not formed so readily or they are not so easily converted into amido compounds, and the heat produced by the reaction when phenol is used is the cause of the loss of some nitric acid. Furthermore, phenol and benzoic acid do not break up so easily in the final reaction, and therefore it takes longer to complete the oxidation than when salicylic acid is used.

Other nitro- and amido-forming compounds might be substituted for salicylic acid, but its use makes the method so simple and accurate that it is doubtful whether any other substance would improve it. Other substances have been tried, *e. g.*, pure potassium nitrate, with gallic acid in the place of salicylic acid, gave 6.68 per cent of nitrogen; pyrogallie acid, 8.21 per cent; phenol, 13.62 per cent; benzaldehyde, 13.62 per cent; and phenyl salicylate, 13.72 per cent. It is interesting to note that phenyl salicylate gave satisfactory results, but the oxidation is not so rapid as when salicylic acid is used. For ease in manipulation, rapidity of work, and accuracy of results the salicylic acid method is to be recommended.

Official Kjeldahl Method for Nitric Nitrogen.—As stated previously, the presence of certain organic compounds rich in hydrocarbons permits the reduction of nitric nitrogen to ammonia by combustion with sulfuric acid. Benzol, phenol, and salicylic acid have been used for this purpose. The official chemists have adopted the salicylic acid process first proposed by Scovell.¹

Gunning and Voorhees Methods for Nitric Acid.—The essential features of this modification are due to Winton and Voorhees.² The modifications of the Kjeldahl method, for similar purposes, furnished the following material details for the modified Gunning process.

Digest for 2 hours in a 0.5 liter flask from 0.5–1 gram of the sample with 30 cc. of sulfuric acid containing 2 grams of salicylic acid. Slowly add, with constant shaking, 2 grams of zinc dust and heat the flask, at first gently, until, after boiling a few minutes, dense fumes are no longer emitted. Add 3 grams of potassium sulfate, and continue the boiling until the solution is colorless, or, if iron is present,

¹ The details are given in *Methods of Analysis*, A. O. A. C.

² Connecticut Agr. Exp. Sta. Bull. **112**, 3; U. S. Dept. Agr. Div. Chem. Bull. **35**, 86.

until a light straw color is produced. On cooling, when the mixture begins to solidify, add water with caution and afterwards sodium hydroxide, and obtain the ammonia by distillation.

The Voorhees process is superior to that recommended by Winton in that it adds the potassium sulfate at the beginning of the combustion. It is conducted as follows:

Digest the sample with 10 grams of potassium sulfate, 30 cc. of sulfuric containing 1 gram of salicylic acid, and 3 grams of zinc sulfide. Keep down the heat until frothing ceases, and then keep the mass in the gentle ebullition until clear. Take the usual precautions in making the distillation.

Sources of Error.—Continual vigilance is necessary to secure accurate results, especially if nitrates are present in the fertilizer. No dependence can be placed on running two portions of the same substance at the same time, since the same error may affect both portions, and there is also the psychological error to be considered. It is best to run the checks at different times, and in the meantime forget the previous results. Some of the sources of error are (1) leaks in the condensing system; (2) digestion carried too low; (3) distillation carried too low; (4) nitrates not dissolved before reagents are added; (5) too much heat evolved in the beginning of the digestion when nitrates are present; (6) inaccurately standardized solutions; (7) reagents containing nitrogen—they should frequently be tested by a blank with sugar.

A. O. A. C. Work on the Kjeldahl Method Modified for Nitrates.—The Kjeldahl method modified for nitrates by the use of salicylic acid was studied by M. A. Scovell,¹ referee in 1889, in collaborative work in comparison with the Ruffle method. E. B. Voorhees,² in 1890, continued the study and recommended the use of zinc sulfide as a reducing agent in place of zinc. In 1891 William Frear³ studied the use of sodium thiosulfate as a reducing agent. In 1893 C. L. Parsons⁴ reported on the Gunning method modified for nitrates by the use of salicylic acid. This method was adopted that year; the use of sodium thiosulfate as a reducing agent was also adopted. J. M. Bartlett,⁵ in 1894, made comparative studies of the estimation of total nitrogen including nitrates by both the Kjeldahl and the Gunning methods modified for nitrates.

¹ U. S. Dept. Agr. Div. Chem. Bull. **24**, 85.

² *Ibid.*, **28**, 10.

³ *Ibid.*, **31**, 117.

⁴ *Ibid.*, **38**, 41.

⁵ *Ibid.*, **43**, 136.

In 1908 C. L. Penny¹ studied the estimation of nitrogen in mixed fertilizers containing nitrates. C. H. Jones,² referee in 1909, made a study of 6 variations of the salicylic acid method, 19 analysts in 16 laboratories taking part in the work. The variations concerned the time of standing after adding the acid and after adding the zinc dust or thiosulfate for the reduction. The general tendency seemed towards slightly higher figures when the material stood 6 hours, though some chemists report similar results by all procedures.

Precautions Necessary in the Kjeldahl Method Modified for Nitrates.—

The sample must be covered completely and quickly by the sulfuric acid-salicylic acid mixture. Nitric acid is set free when the acid comes in contact with the nitrate, and if this acid is not absorbed, the results will be too low. Both the sample and the flask should be dry. The presence of moisture increases the heat of reaction and thus increases the danger of volatilization of nitric acid before it is absorbed.

A sufficient quantity of the salicylic acid must be used. The nitrates should be dissolved and the nitric acid should enter into reaction with the salicylic acid before the reducing agent is added. This may require a little time, especially if the sample is not finely ground. Rudnick suggests heating the flask slightly, when any undissolved nitrate dissolves with a crackling sound. In such case, however, the liquid should be cooled before the reducing agent is added.

The necessary precautions with respect to standard solutions, distillation, etc., of the Kjeldahl method should also be considered in this connection.

Study of the Kjeldahl Salicylic Acid Method by Moore.—H. C. Moore³ reports a study of some of the factors of this method.

Digestion.—The important considerations are the length of the digestion period, the rate of boiling or amount of heat applied, and the quantities of reagents employed. It is noted that at least 45-50 cc. of salicylsulfonic acid is required for 0.8517 gram of sodium nitrate and that at least 4-8 hours of gentle boiling and the use of 5 grams of potassium sulfate and 0.5 gram of mercury are required for digestion. It is noted further that by using 10 grams of potassium sulfate and 1 gram of mercury, digesting at a brisk boil 1 hour after solution has become clear is sufficient.

¹ U. S. Dept. Agr. Div. Chem. Bull., **122**, 85.

² *Ibid.*, **132**, 16.

³ *J. Ind. Eng. Chem.*, **12**, 669 (1920).

Proportion of Reagents.—From the reaction it may be calculated that 1 gram of sodium nitrate requires 1.64 grams of salicylic acid. In various text-books it is stated that from 0.25 to 5 grams of nitrate may be taken with 30-35 cc. of sulfuric acid and 2 grams of salicylic acid. From this it may be understood that some analysts have used too little salicylic acid to obtain concordant and correct results. It was found that for a 0.5 gram sample, 35 cc. of salicylsulfonic acid, containing 1 gram of salicylic acid, gave correct results. It thus appears that the proportion of reagents is very important. At least 45 cc., and preferably 50 cc., of the salicylsulfuric acid is required for a 1 gram sample, and for a 1.7034 gram sample, 70 cc. is required. Why it is necessary to use so great an excess of acid with the increase in the sample is not apparent.

Some determinations were made with 0.5 gram of copper sulfate; the few results obtained were slightly less concordant. The same applies when 0.5 gram each of mercury and copper sulfate was used. Copper sulfate offers no advantage over mercury and seems slower in action. Sodium sulfate was found to give the same results as did potassium sulfate. The addition of 0.1-0.5 gram of sodium chloride had no effect on the accuracy of the method.

The use of moist samples was tested by adding from 0.1 to 0.5 cc. of water, but the results were unchanged. At times, however, adding the salicylsulfonic acid to moist samples caused some heating, and puffs of nitric acid could be noted. Therefore dry samples are preferred. If not dry, the sample may be dried after weighing by rotating the flask over a low heat. There would also be danger of decomposing ammonium nitrate, if heated too much. Warming after adding the salicylsulfonic acid, gave slightly lower results, amounting to from 0.04 to 0.08 per cent nitrogen.

Devarda-Kjeldahl Method.—A method proposed by Davisson and Parsons¹ is especially suitable for total nitrogen in solutions containing organic matters and nitrates. It is a combination of the Devarda and the Kjeldahl methods. The nitrates are reduced in alkaline solution by Devarda's alloy, and the ammonia is absorbed in a special tube containing sulfuric acid, which is attached to the flask. The method is fully described as follows:

The reduction is carried out in a flask connected with an absorbing tower (Fig. 4). During the reduction, the large volume of hydrogen evolved before the

¹ *J. Ind. Eng. Chem.*, **11**, 306 (1919).

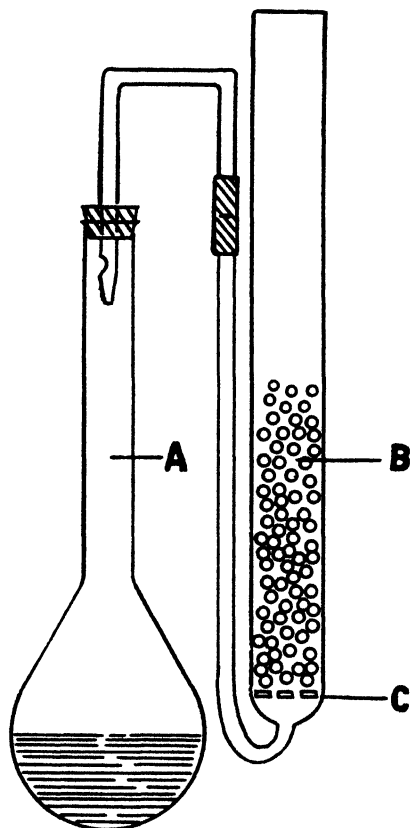


Fig. 4.—Davisson-Parsons Absorption Apparatus.

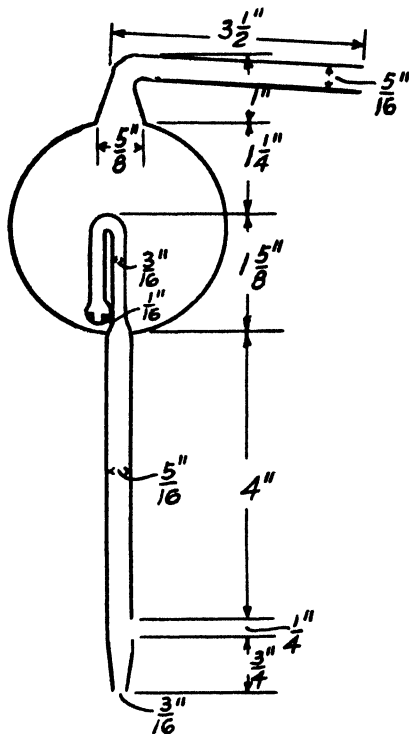


Fig. 5.—Davisson Scrubber.

solution boils sweeps out with it some ammonia, and this ammonia is difficult to scrub from the mixture of air and hydrogen. An absorption tower readily overcomes the difficulty, the hydrogen being completely scrubbed as it passes through the acid in the tower. The tower should be about $1\frac{1}{4}$ – $1\frac{1}{2}$ inches in diameter and 14 inches long. (Fig. 5). *A* contains the nitric solution, *B* is a 6 inch column of glass balls or broken glass rods about $\frac{1}{4}$ inch in length, and *C* is a small perforated plate which may be porcelain or made from a rubber gasket. The tower is easily washed after the reduction is complete. The tendency of solutions high in organic matter to foam when reduction is made in an alkaline solution can be overcome by using about 4 drops of ordinary lubricating oil, the oil being easily destroyed subsequently in the Kjeldahl digestion.

In the absorbing tower are placed 35 cc. of sulfuric acid (4 + 1). The solution, 100–200 cc. in volume, is placed in a 500 cc. Kjeldahl flask, and sufficient 50 per cent sodium hydroxide is added to make the strength of the solution 0.1 *N* in sodium hydroxide. This sodium hydroxide solution should be measured carefully.

To the solution are added 4 drops of oil and 1 gram of Devarda's alloy (60-mesh, made free from ammonia by heating it to about 200° C. for 30 minutes), and the flask is connected with the tower. The solution is heated to boiling as quickly as possible and kept boiling gently for 20 minutes, during which time the acid in the tower just about reaches the boiling temperature. The flame is now removed, and the acid is allowed to suck back into the flask, after which the solution is boiled for a few minutes and the flame removed. The tower is then washed with small quantities of distilled water, and the water is permitted to suck back into the flask. Four washings with about 25 cc. each of water are sufficient to remove all the ammonia from the tower. The solution is now evaporated to charring, 5 grams of potassium sulfate is added, and the digestion is continued for about 1 hour after becoming bluish. After digestion is complete, the ammonia is distilled after strong caustic soda carrying potassium or sodium sulfide has been added. It is necessary to add a relatively large excess of alkali before distilling.

The foaming present during the reduction of the nitrates in the presence of organic matter may be overcome by placing the sample in a beaker, adding 50 cc. of water, heating to boiling, filtering through a small nitrogen-free filter paper into a 500 cc. Kjeldahl flask, and washing the residue and beaker several times with hot water. The nitrates are now in solution and are reduced as outlined above. After the reduction is complete and the water is boiled off, the filter paper with the residue is added to the flask, together with 5-7 grams of potassium sulfate, the mass is digested, and the ammonia is determined in the usual manner.

Jacobs and Gildert¹ tested the Davisson-Parsons method and applied it to mixtures containing nitrates and cyanamides. They proposed the following modifications for such mixtures:

Place the sample in an 800 cc. Kjeldahl flask, add 100-200 cc. of distilled water and sufficient sodium hydroxide (1 + 1) to make the solution 0.1 *N*. Add sufficient Devarda's alloy (Cu-50, Al-45, Zn-5) to reduce all the nitrate nitrogen. (1 gram of alloy will reduce about 25 mg. of nitrate nitrogen.) Connect the flask to a Davisson-Parsons absorption tube containing 35 cc. of sulfuric acid (4 + 1), reduce the nitrate nitrogen to ammonia, and allow the acid in the absorption tube to suck back into the flask. Wash the tube thoroughly with distilled water. Evaporate the solution to charring, add 5-7 grams of potassium sulfate, and continue the digestion for about 1 hour after the melt has become clear. Then cool the melt, dilute and distil.

After comparison with the other methods, the various investigators cited by Jacobs and Gildert are almost unanimous in the opinion that more uniform and reliable results can be obtained under a wider variety of conditions by the use of Devarda's alloy than with any of the other proposed methods. The majority of the workers cited used either the Davisson-Parsons procedure or a slight modification of it.

¹ *Ind. Eng. Chem.*, **14**, 1045 (1922).

HYDROLYSIS OF CERTAIN SYNTHETIC ORGANIC COMPOUNDS

The hydrolysis of certain organic compounds of various constitutions in the Kjeldahl method was studied by Phelps and Daudt.¹ In the presence of 0.7 gram of mercuric oxide or with 0.7 gram of mercuric oxide, 8.2 grams of sodium sulfate, 20 cc. of sulfuric acid, 10 grams of potassium sulfate and 25 cc. of sulfuric acid, weights of the compound varying from 0.2 to 0.4 gram were hydrolyzed completely by heating at the boiling point for 2½ hours. The hydrolysis was found to be complete for the following compounds:

Glucosamine hydrochloride	Isoquinoline derivatives:
Tetramethylammonium derivatives:	Papaverine
Tetramethylammonium iodide	Narcotine
Choline hydrochloride	Morphine
Pyrrol derivative:	Hydrastinine
Isatine	Purine derivative:
Pyrrolidine derivatives:	Caffeine
Atropine	Imidazole or glyoxaline derivatives:
Cocaine	Lophine
Pyridine derivatives:	Amarine
Nicotine zinc chloride	Histidine dihydrochloride
Nicotinic acid	Quinoxaline derivative:
Piperidine derivative:	Quinoxaline hydrochloride
β-Eucaine hydrochloride	Quinazolon derivatives:
Quinoline derivatives:	2-Methyl 4-quinazolon
Hydroxyquinoline	2-Methyl 3-phenyl 4-quinazolon
Cinchonidine	
Strychnine	
Brucine	

Nitrogen in Azo Compounds.—Phelps and Daudt² found that azo compounds were not completely hydrolyzed to ammonia by digestion with 0.7 gram of mercuric oxide, 10 grams of potassium sulfate and 25-30 cc. of sulfuric acid, whether applied directly or after preliminary treatment with zinc dust, salicylic acid and sulfuric acid, with zinc dust and sulfurous acid solution or with a mixture of fuming sulfuric acid and sulfur. When the preliminary treatment included solution in 20 cc. of alcohol and reduction with zinc dust and hydrochloric acid, the results were in fair accord with the theory. The hydrochloric acid reacted so slowly with the zinc that from 0.2 to 0.4 cc. of stannous chloride solution, consisting of 40

¹ *J. Assoc. Official Agr. Chem.*, **3**, 218 (1919); **4**, 74 (1920).

² *Ibid.*, **3**, 306 (1920).

grams of stannous chloride in 100 cc. of concentrated hydrochloric acid, was added to hasten the action. The mixture was kept boiling for 15 minutes, or for 7 minutes after decolorization. Glass return condensers of a modified Hopkins type were placed in the neck of the flasks to prevent the evaporation of alcohol. After cooling, an equal volume of water and 30 cc. of sulfuric acid were added, and the mixture was heated until the water had been expelled and foaming had ceased. After the addition of 0.7 gram of mercuric oxide and 10 grams of potassium sulfate the hydrolysis was conducted at the boiling point.

Reduction with stannous chloride in alcoholic solution was more efficacious. The azo compound was dissolved in 20 cc. of alcohol; 5 cc. of stannous chloride solution, containing 40 grams of stannous chloride in 100 cc. of hydrochloric acid, was added, and the mixture was kept at the boiling point for 15 minutes if bleaching was completed in 7 minutes or less.

The results just mentioned were received with the following compounds: Azobenzene, hydroxyazobenzene, aminoazobenzene, toluene azo, p-toluidin, methyl red, diethyl red, dipropyl red, benzene azo, β -naphthylamine, ponceau 4 R, and congo red.

Nitrogen in Hydrazine Compounds.- Phelps and Daudt also observed that hydrazine sulfate and semicarbazide hydrochloride were not completely hydrolyzed by digestion with 0.7 gram of mercuric oxide, and with 10 grams of potassium sulfate and 25-30 cc. of sulfuric acid, whether applied directly or after preliminary treatment with stannous chloride or with zinc and hydrochloric acid; or by formation of hydrazine derivatives of glucose in the presence of sodium acetate and water; or by reduction of these compounds obtained as above with stannous chloride, sodium amalgam or sodium formate. When zinc dust and acetic acid were employed, the results indicated complete hydrolysis.

The procedure followed below seemed to be applicable to hydrazine, phenylhydrazine and phenylmethylhydrazine compounds, but not to semicarbazide or oxamazide. The nitrogen compounds were dissolved in water; glucose, glacial acetic acid and zinc dust were added in the order mentioned; and the mixture was kept at the boiling temperature for 1 hour under a return condenser of the Hopkins type. Upon cooling, 30 cc. of concentrated sulfuric acid was added, and the mixture was carefully heated until the water had been evolved and foaming had entirely ceased. Then 0.7 gram of mercuric oxide and 10 grams of potassium sulfate were added, and the hydrolysis was conducted at the boiling temperature.

The following method was found to be of more general application: Alcoholic solutions of the nitrogen compounds were treated with formaldehyde solution, zinc dust and hydrochloric acid. The mixture was kept at the boiling temperature for 30 minutes or more under a return condenser. After the reduction had progressed for 15 minutes a small quantity of stannous chloride solution was added for the purpose of hastening the action of the acid on the zinc. After cooling an equal volume of water and 30 cc. of sulfuric acid were added. When the water had been expelled, the hydrolysis was conducted in the usual manner with mercuric oxide and potassium sulfate.

The method gave results in accord with the theory if reduction of the aldehyde nitrogen complex to the amino compound was complete. It appeared that the variability in the results was due to the impurity in the zinc dust rather than to the method. It seems to be a matter of some difficulty to obtain a supply of uniformly pure zinc dust. Oxide in the free metal or hydrolyzable nitrogen-containing compounds, or both, present in the zinc dust in varying quantities, often make it impossible to find a sufficiently uniform sample. A proper state of subdivision is also an important factor in the efficacy of the zinc when used as the reducing agent.

Following is a list of the compounds used to obtain the results mentioned:

Hydrazine sulfate, phenylhydrazine hydrochloride, bromphenylhydrazine, methylphenylhydrazine sulfate, diphenylhydrazine hydrochloride, p-nitrophenylhydrazine, phenylbenzoylhydrazine, diphenylbenzoylhydrazine, semicarbazide hydrochloride, phenylsemicarbazide, and oxamazine.

NITROGEN IN THE FORM OF AMMONIA OR NITRATES

Nitrogen as Ammonia.—The most frequent form in which ammonia is used for fertilizing is as the sulfate. The method of determination to be described, however, is equally applicable to all ammonia salts. When no other form of nitrogenous compound is present the ammonia can be easily and directly determined by distillation with soda- or potash-lye.

To 1 gram of the ammonia salt add from 200 to 300 cc. of water and 30 grams of the soda-lye used in the moist combustion process; distil, collect the ammonia, and titrate the excess of sulfuric acid.

Fresenius recommends that the ammonia expelled by distillation be taken up by a standard solution of sulfuric (hydrochloric, oxalic) acid, the excess of which is titrated with a standard solution of soda or other alkali, litmus being used as an indicator. If on examination the distillate is found to contain thiocyanate, caustic magnesia is applied in place of

soda-lye for the expulsion of ammonia, because soda decomposes thiocyanate with the production of some ammonia.

In all cases where organic matter containing nitrogen is present, caustic magnesia must be substituted for the soda solution. The magnesia must be added in sufficient excess and the distillation continued a little longer than is necessary when soda-lye is used. Otherwise the details of the operations are the same. In a mixed fertilizer containing only organic nitrogen and ammonia salts, the total nitrogen can be determined by the moist combustion process, and the ammoniacal nitrogen by distillation with magnesia. The difference between the two results will give the nitrogen due to the organic matter.

To avoid any possible danger of decomposing organic nitrogenous compounds, the ammonia may be determined in the cold under a bell-jar containing some set sulfuric acid by treatment with soda-lye. The operation should continue for many days, and even then it will be found that some ammonia is still escaping. It may be finally inferred, therefore, that all the nitrogen as ammonia is not obtained by this process or that even magnesia may gradually convert other nitrogenous compounds into ammonia. The method for the estimation of ammonia by distillation with magnesium oxide was adopted by the A. O. A. C. in 1891. It was not subjected to collaborative study.

Thiocyanates in Ammoniacal Fertilizers.—The extended use of ammonium sulfate as a fertilizer renders it important to determine the actual constituents that may be present in samples of this material. The following bodies have been found in the soluble portions of commercial ammonium sulfates: sulfuric acid, chlorine, ammonia, thiocyanic acid, potash, soda, lime and iron oxide. In the insoluble portions have been found silica, sulfates, lime, magnesia and iron oxide. A sample of commercial ammonium sulfate analyzed by Jumeau¹ contained the following substances:

	Per cent
Moisture	10.51
Ammonium sulfate	67.84
Ammonium thiocyanate	9.39
Sodium sulfate	0.24
Potassium sulfate	0.98
Calcium sulfate	0.68
Iron thiocyanate	0.50
Magnesium chloride	traces
Silica	0.07
Undetermined	0.77

¹ *Rev. chim. appliquée*, 1, 51 (1893).

The determination of the thiocyanic acid in the thiocyanate is generally made by the oxidation of the sulfur to sulfuric acid and its subsequent weighing in the form of barium sulfate. Juneau modified the method by determining the quantity of the thiocyanate by means of a titrated liquid. The method is as follows:

Prepare a solution of ammonium thiocyanate containing 8 grams of this salt per liter, and determine its exact content of thiocyanate by titrating with silver nitrate or by the weight of the barium sulfate produced after the oxidation of the sulfur. Dilute 10 cc. of the titrated liquor with water to about 100 cc. and add 10 cc. of pure sulfuric acid. Then add, dropwise, a solution of potassium permanganate containing about 10 grams of that salt per liter. The permanganate is instantly decolorized. Evolution of hydrocyanic acid occurs as the thiocyanate passes to the state of sulfuric acid. A single drop in excess gives to the mixture the well-known rose coloration of the permanganate solution which persists for several hours. The number of cubic centimeters necessary to produce the persistent rose tint is noted, and the same operation is carried on with 0.5–1 gram of the unknown product that is to be assayed. A simple proportion indicates the content of the thiocyanate in the unknown body. The process is of great exactitude and permits the rapid determination of thiocyanic acid in the presence of chlorides, cyanides, etc., which remain without action upon the permanganate. If chlorides and cyanides are absent, the thiocyanate can be determined directly by silver nitrate either by weighing the precipitate or by the process of Volhard, which is based upon precipitation of the silver by thiocyanate in the presence of a ferric salt. The end of the reaction is indicated by the red coloration shown by the liquid when the thiocyanate is in excess.

DETERMINATION OF NITRIC NITROGEN BY REDUCTION TO AMMONIA

When nitrogen is present in a highly oxidized state, *e. g.*, as nitric acid, it may be quickly and accurately estimated by reduction to ammonia. One way to do this is by utilizing the reducing power of nascent hydrogen. This substance may be secured in the active state by the action of an acid or alkali on a metal or by means of an electric current. The processes depending on the use of a finely divided metal in the presence of an acid or alkali have come into general use within a few years, and they are now employed generally instead of combustion with copper oxide or the colorimetric method with indigo.

The typical reaction that takes place in all cases is represented by the following equation: $2\text{HNO}_3 + 8\text{H}_2 = 2\text{NH}_3 + 6\text{H}_2\text{O}$.

The method will be considered under three heads: (1) Reduction in an alkaline solution; (2) reduction in an acid solution; (3) reduction by means of an electric current.

In an alkaline solution the reduction and distillation may proceed together. In acid solutions the reduction is followed by the distillation after the addition of an alkali. In the third class of operations the reduction is accomplished by means of an electric current, and the ammonia is subsequently obtained by distillation or determined by nesslerizing. These processes may be applied to the nitrates or nitrites as such, or as occurring in rain and drainage waters and soil extracts. Owing to the ease with which the analyses are accomplished, the short time required and the accuracy of the results, these reduction methods for nitrates commend themselves to analysts.

Halle Zinc-Iron Method.—For determining the nitrogen in Chile salt-peter the method as conducted at the Halle Station is as follows:

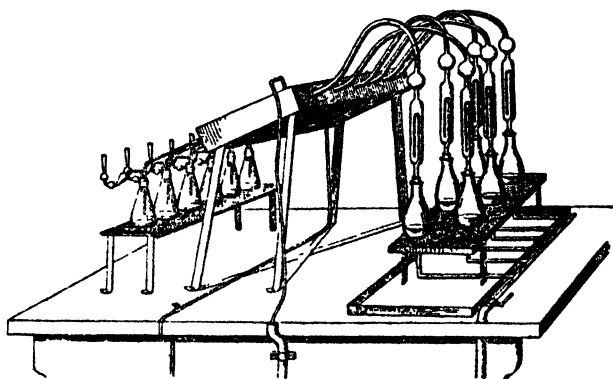


Fig. 6.—Halle Nitric Acid Apparatus.

Dissolve 10 grams of the nitrate in 1 liter of water and use 50 cc. of the solution corresponding to 0.5 gram of the sample for each determination. The apparatus employed is shown in Fig. 6. A mixture of 5 grams of zinc dust and an equal weight of iron filings is used as the source of hydrogen. The reduction takes place in an alkaline medium secured by adding to the other materials mentioned 80 cc. of soda-lye, sp. gr. 1.30. The respective quantities of iron and zinc may be measured instead of weighed, as exact proportions are not required. After the addition of all the materials allow the flask to stand for 1 hour at room temperature and then distil, using some kind of safety arrangement to prevent the particles of soda-lye being carried over by the hydrogen evolved. The siphon bulb shown in the figure is effective for this purpose.

Better results are obtained by condensing the escaping steam with water. When the condensed liquid collects in considerable quantities in the safety tube, raise the tube so it will not dip in the liquid in the receiver, and extinguish the lamp under

the flask to permit the return of the liquid to the flask by means of the siphon. Repeat two or three times during the process of the distillation to prevent a too high concentration of the soda-lye to endanger the flask. Determine the excess of acid in the receiver by titration, as in the regular Kjeldahl method. Make blank determinations from time to time and corrections in harmony therewith.

Devarda Method.—The slow action arising from the use of pure metals in the reduction of nitrates to ammonia has been overcome, to some extent, by Devarda,¹ by use of a finely powdered alloy consisting of 45 per cent of aluminum, 50 per cent of copper, and 5 per cent of zinc. In dissolving, the copper is left in a finely divided state, which helps to prevent bumping in distillation. The analytical process is carried out as follows:

Place a quantity of the solution containing the nitrate, equivalent to about 0.5 gram of potassium nitrate, in a flask having a capacity of about 1 liter, dilute with 60 cc. of water and 5 cc. of alcohol, and add 40 cc. of caustic potash solution, sp. gr. 1.3. Introduce from 2 to 2.5 grams of the alloy described above and attach the flask to a condenser with a receiver containing standard acid. Make the connection between the flask and the condenser by means of a tube having on the limb next the flask a bulb filled with glass beads to prevent the contents of the flask splashing over into the receiver, and on the other limb another bulb to prevent the acid in the receiver finding its way into the distillation flask, should regurgitation occur. When the flask has been connected with the condenser, heat it gently for half an hour, at the end of which time the evolution of hydrogen will have slackened or ceased; distillation then proceeds, cautiously at first, until the zinc of the alloy has completely dissolved, and then more vigorously, for about 20 minutes after boiling starts. Collect the distillate in standard acid and determine the ammonia by titration of the residual acid in the ordinary way.

The strength of the alkali is of importance. If too strong, the action of the alloy is unduly vigorous at the beginning. If it is too weak, the contents of the flask have to be overheated, the result in either case causing the formation of a fine spray of caustic solution. With the right strength of alkali (42 per cent by weight, sp. gr. 1.453) the spray is at a minimum, and a Davison scrubber absorbs what is produced.

The results secured by a large number of collaborators working with Prince² and using the Devarda alloy method on commercial samples of nitrates indicate that the method is quite satisfactory. Previous collaborative work done in 1921 and again in 1922 showed that the method was satisfactory for pure nitrates. The Devarda method was studied by the referee in 1921, 1922 and 1923. It was adopted as official in 1923 and it is published in *Methods of Analysis, A.O.A.C.*

¹ *Chem. Z.*, **16**, 1952 (1892).

² *J. Assoc. Official Agr. Chem.*, **3**, 410 (1925).

Arnd Method.—The Arnd method is similar to the Devarda method in that the nitrate is reduced by an alloy and distilled into standard acid. The procedure is as follows:

Dissolve 10 grams of the nitrate in distilled water free of carbonic acid and make up to 500 cc. Pipet 25 cc. (1.0 gram) into a distillation flask and add 200 cc. of water and 10 grams of freshly granulated Arnd's alloy (40 per cent of magnesium and 60 per cent of copper). Add 50 cc. of 20 per cent magnesium chloride solution through a dropping funnel and distil until about 50 cc. remains in the flask. Make the distillation through a block tin condenser in the usual way and collect in a receiver containing 40-50 cc. of sulfuric acid. Titrate the excess acid with standard caustic soda.

The referee in 1927 found the method to be simple and accurate for nitrate salts alone, but to have no distinct advantage over the Devarda method. Like the Devarda method it is not suitable for use in the presence of organic materials.

Ferrous-Sulfate-Zinc-Soda Method.—The ferrous-sulfate-zinc-soda method depends upon reduction of nitrates in alkaline solution by means of ferrous sulfate and zinc. It was proposed by Salle and brought to the attention of the A. O. A. C. in 1911.¹ The referee in 1913 (C. L. Hare) subjected it to collaborative study and it was adopted provisionally² that year and finally in 1916.²

Ulsch Method.—The method of Ulsch³ uses reduced iron. The procedure is as follows:

Dissolve 0.5 gram of saltpeter or 0.4 gram of sodium nitrate in 25 cc. of water, in a flask with a content of about 600 cc. Add 5 grams of iron reduced by hydrogen and 10 cc. of sulfuric acid diluted with two volumes of water. To avoid mechanical losses during the evolution of hydrogen, hang a pear-shaped glass stopper in the neck of the flask. After the first violent evolution of hydrogen has passed, gradually reheat the flask until it is brought to a gentle boil (approximately 4 minutes). Continue the boiling for about 6 minutes, when the reduction is complete. Add 50 cc. of water, an excess of soda-lye, and a few particles of zinc. Distil the ammonia and collect in standard acid in the usual way.

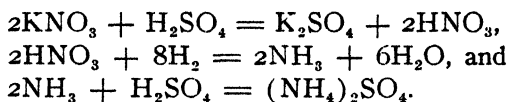
Errors may be caused by reduced iron containing nitrogen, therefore a blank should be made on a new lot of the reagent.

¹ U. S. Dept. Agr. Div. Chem. Bull., **152**, 28.

² *J. Assoc. Official Agr. Chem.*, **1**, 100 (1915); **3**, 520 (1920); *Methods of Analysis, A.O.A.C.*

³ *Chem. Zentr.*, **2**, 926 (1890).

The method of Ulsch has usually given satisfactory results. It is based on the following reactions :



Zinc Iron Method.—The zinc iron method, which at one time was official, is similar to the Ulsch method previously described, but it is intended for the estimation of the quantity of nitrates in mixed fertilizers. It was studied by the referee in 1893 and in 1894 and adopted in 1894. The use of urea and calcium cyanide in mixed fertilizers rendered the method inaccurate, and it was discarded in 1928.¹ The method is suitable for nitrate salts, but other methods are available.

REDUCTION BY ELECTRIC CURRENT

Williams-Warington Method.—This process is applicable to solutions or extracts of fertilizers, soils, etc., and rain or drainage waters containing only a small quantity of nitrates. Following his observations of the losses which naturally occur during the evaporation of water, even with all the precautions usually observed, Warington² was led to try some method for the determination of nitrates and nitrites in waters without previous concentration. The reduction of these bodies by the copper-zinc couple formed the basis of these experiments, and they resulted in the following method of manipulation, which is based on the following process devised by Williams.³

Distil rapidly 1 liter of the solution of a fertilizer or rain water with a little magnesia which has been previously raised to a low red heat and then washed, until 250 cc. has distilled. Make up the residue to 800 cc., transfer to a wide-mouthed, stoppered bottle supplied with strips of copper and zinc forming electric couples, and set aside, at a temperature of from 21° to 24° C. for 3 days. Then distil a measured portion of the solution and determine the ammonia in the distillate by nesslerizing.

The ammonia, as well as the nitrogen as nitrates and nitrites, can be determined in the course of the same operation and in the same sample of the solution. For this purpose it is only necessary to fit the distilla-

¹ *J. Assoc. Official Agr. Chem.*, **12**, 70 (1929).

² *J. Chem. Soc.*, **55**, 538 (1889).

³ *Ibid.*, **39**, 100 (1881).

tion flask to a condenser and to remove all ammonia from the apparatus by boiling distilled water in the retort before introducing the solution. The distillate of 250 cc., obtained as described above, is well mixed and the ammonia is determined in from 25 to 100 cc. thereof, diluted to 150 cc. with ammonia-free water. The nitrogen, as nitrates and nitrites, is determined directly and alone. The error of the determination is as small as nesslerizing admits of, since it is possible, if necessary, to distil until the full amount of ammonia is obtained.

THE NITRIC OXIDE PROCESS

Schloesing Method.—The principle of the Schloesing¹ method depends on the decomposition of nitrates in the presence of a ferrous salt and a strong mineral acid. The nitrogen appears as nitric oxide, the volume of which may be measured directly, or it may be converted into nitric acid and titrated by an alkali. The typical reactions that take place are represented by the following equation:

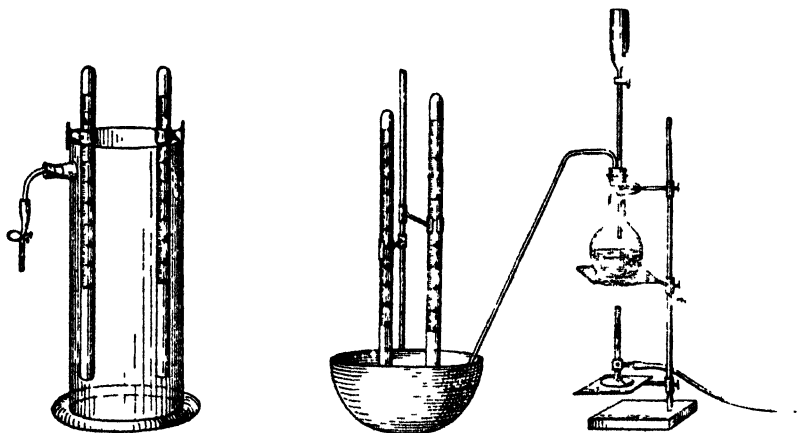
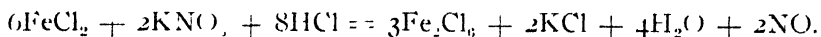


Fig. 7.—Schloesing-Wagner Apparatus.

Schloesing-Wagner Method.—The Schloesing-Wagner method for estimating nitrogen in the nitrates of fertilizers is carried out at the Halle experiment station as follows:

Provide a flask, Fig. 7, of about 250 cc. capacity with a rubber stopper with two holes; through one of them pass the stem of a funnel carrying a glass stop-

¹ *Z. anal. Chem.* 9, 24 (1870).

cock and through the other a delivery tube that leads to the receiving vessel. The end of the delivery tube is bent so as to pass easily under the mouth of the measuring buret and is covered with a piece of rubber tubing.

Place 50 cc. of saturated ferrous chloride solution and the same quantity of 10 per cent hydrochloric acid in the flask. (The ferrous chloride solution is obtained by dissolving nails or other small pieces of iron in hot hydrochloric acid, and it is kept in glass-stoppered flasks of about 50 cc. capacity, entirely filled. The contents of one flask are enough for about 12 determinations and by using the entire contents of a flask as soon as possible after opening any danger of oxidation, which might take place in a large flask, is avoided.) Boil the contents of the flask until all the air is driven off. Then place the delivery tube under the measuring tube, which is filled with 40 per cent potash-lye and covered with a piece of filter paper. By careful and quick inversion bring the measuring tube into the vessel receiving it without allowing any air to enter. Continue the boiling for some time, and when no more air escapes bring the end of the delivery tube into another freshly filled measuring tube, and begin the estimation. Place 10 cc. of a saltpeter solution, containing 2.5 grams of pure sodium nitrate in 100 cc., in the funnel, and with continued boiling allow it to pass, drop by drop, into the flask. When almost all the solution has run out wash the funnel three times with 10 cc. of 10 per cent hydrochloric acid and allow it to pass, drop by drop, into the flask. When no more nitric oxide is evolved transfer the measuring tube to a large jar filled with distilled water.

The solution of the substance to be examined should be used in such quantity as will give about the same quantity of gas as is furnished by the 10 cc. of test nitrate solution described previously, that is, about 70 cc. Eight or ten determinations can be made, one following the other, and finally another determination with normal sodium nitrate solution should be made as a check. At the end of the operation all the measuring tubes are in the large jar filled with distilled water. The temperature of the surrounding water will soon be imparted to the contents of each tube, and the volume of nitric oxide is read by bringing the level within and without the measuring tube to the same point. The percentages are calculated for the given temperature and barometric pressure in the usual way; or to avoid computation, the volume can be compared directly with the volume furnished by the normal nitrate solution, which is a much simpler method.

Schulze-Tiemann Method.—The modification by Schulze-Tiemann¹ of the ferrous salt method consists chiefly in the omission of the use of carbon dioxide and in the simplified form of apparatus, which permits rapid work and also gives, according to some authorities, exact and reliable results. Their procedure is as follows:

¹ *Z. anal. Chem.*, 9, 24, 401 (1870).

Reduce the extract representing 500 grams of the fine soil by evaporation to 100 cc. and place in a glass flask, *A* (Fig. 8), of 500 cc. capacity. Close the flask with a rubber stopper with two bent glass tubes passing through it. The delivery tube is drawn out into a point at *a* and reaches about 2 cm. below the surface of the rubber stopper. The tube *efg* passes just to the lower surface of the rubber stopper. The flask is connected by means of rubber tubes and pinch-cocks with the tubes *d* and *h*. The pinch-cock at *c* and *g* must be capable of closing the tubes

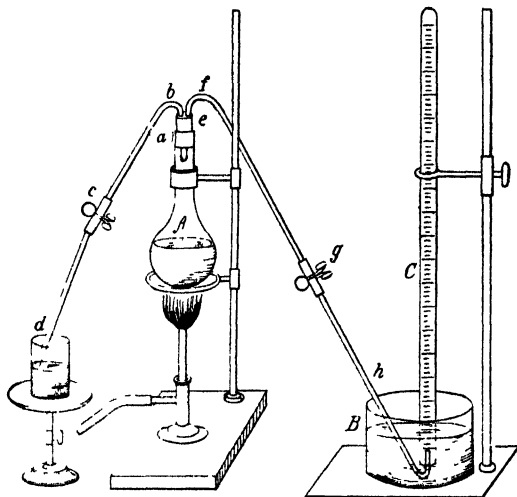


Fig. 8.—Schulze-Tiemann Nitric Apparatus.

air-tight. The end of the tube *gh* passes into a crystallizing dish, *B*, and is bent upward to a point passing 2 or 3 cm. into the measuring tube *C*. The point within the tube is covered with a piece of rubber tubing. The measuring tube *C*, together with the crystallizing dish, *B*, is filled with a 10 per cent solution of boiled soda-lye, which is obtained by dissolving 12.9 parts of sodium hydroxide in 100 parts of water.

The liquid that is to be examined for nitric acid (the pinch-cocks being opened and the tube *gh* not dipping into the crystallizing dish), is boiled for 1 hour in order to drive the air out of flask *A*. The end of the tube *h* is then brought into the crystallizing dish containing the sodium hydroxide solution so that the steam from the flask, *A*, escapes partly through the tube *c* and partly through the tube *g*, but does not allow the bubbles to enter the measuring tube *C*. To determine whether all the air is expelled, the pinch-cock at *g* should be closed. The soda-lye will thereupon rise to *g* in case no air interferes. It is best to close the tube at *g* first with the thumb and finger, and then the rise of the soda-lye to that point can be determined by the impulse felt. The tube is then firmly closed by means of the pinch-cock *g*. The rest of the steam is allowed to escape through the tube *c*, and the evaporation is continued until the contents of the flask are evaporated to about 10 cc. The flask into which the tube *c* dips is filled with freshly boiled water. The

lamp is removed from the flask *A*, the pinch-cock is closed, and the tube *c* becomes filled with freshly boiled water. The measuring tube, *C*, filled with freshly boiled soda-lye, is placed over the end of the tube *g*.

The pressure of the external air will now flatten the rubber tubes at *c* and *g*. The flask at the end of *c*, holding freshly boiled water, is then replaced with one filled with a nearly saturated solution of ferrous chloride containing some hydrochloric acid. The flask containing the ferrous chloride solution should be graduated so that the amount that is drawn into flask *A* can be determined.

The pinch-cock *c* is opened and from 15 to 20 cc. of the ferrous chloride solution is allowed to flow into *A*. The end of the tube *c* is then placed in another flask containing strong hydrochloric acid, and the latter is allowed to flow into the tube in small quantities at a time until all the ferrous chloride is washed out of the tube *c* into *A*. At the point *b* there is sometimes formed a little bubble of hydrochloric acid in the form of gas, which entirely disappears when flask *A* is heated.

Flask *A* is next warmed gently until the rubber tubes at the pinch-cocks begin to assume their normal condition. The pinch-cock at *g* is now replaced by the thumb and finger, and as soon as the pressure within flask *A* is somewhat stronger, caused by the nitric oxide gas evolved from the mixture, it is allowed to pass through the tube *g* and escape into the measuring cylinder *C*. By a manipulation of the finger and thumb at *g*, it is possible to prevent regurgitation of the sodium hydroxide into *A*, and at the same time to relieve the pressure of the nitric oxide in *A*, which would be difficult to do by means of the pinch-cock alone.

The boiling of the liquid is continued until there is no longer any increase of the volume of gas in the measuring cylinder *C*. At the end of the operation, the tube *g* is removed from the dish *B* and the measuring tube *C* is closed by means of the thumb while its end is still beneath the surface of the soda-lye, and it is shaken until all traces of any hydrochloric acid that may have escaped absorption are removed. It is then placed in a large glass cylinder filled with water at the temperature at which the volume of gas is to be read. After being kept at this constant temperature for about half an hour the volume of the nitric oxide can be read. For this purpose the measuring cylinder *C* is sunk into the water of the large cylinder until the level of the liquids within and without the tube is the same.

One cubic centimeter of nitric oxide weighs at 0° and 760 mm. barometric pressure 1.343 mg.

Since two molecules of NO (molecular weight 60) correspond to one molecule of N_2O_5 (108), the following equation may be formed: $60 : 108 :: 1.343 : x$. Whence $x = 2.417$ mg., the weight of nitric acid (N_2O_5) corresponding to 1 cc. of nitric oxide.

Merits of the Ferrous Chloride Process.—The possibility of an accurate determination of nitrates, by decomposition with a ferrous salt in presence of an excess of hydrochloric acid, has been established by many years of experience and by the testimony of many analysts. The method is especially applicable when the quantity of nitrate is not too small and when organic matter is present. In the case of minute quantities of nitrate,

however, the process is inapplicable and must give way to some of the colorimetric methods.

In regard to the apparatus, modern practice has led to the preference of that form which does not require the use of carbon dioxide, is the simplest in construction, and that has the smallest cubical content. The evolved gas is most simply measured by collecting it over lye in an azotometer, reading the volume, noting the reading of the barometer and thermometer, and then reducing to standard conditions of pressure and temperature by the customary calculations. When a very strong lye is used, the tension of the aqueous vapor may be neglected. Although every analyst should have a thorough knowledge of the ferrous chloride method and the principles on which it is based, it is not recommended over other methods. It cannot be compared in simplicity to the later methods for nitrates, which are based on the conversion of the nitric acid into ammonia by the action of nascent hydrogen, and in accuracy it does not appear to have any marked advantage over the reduction methods.

Mercury and Sulfuric Acid Method.—This simple and accurate method for the determination of nitric acid in the absence of organic matter is known as the Crum-Frankland¹ process. It is based on the principle of converting nitric acid into nitric oxide by the action of mercury in the presence of sulfuric acid. As first described, the operation was conducted in a glass jar 8 inches long by 1.5 inches in diameter, filled with mercury and inverted in a trough containing the same liquid. The nitrate to be examined, in a solid form, was passed into the tube, together with 3 cc. of water and 5 cc. of sulfuric acid. With occasional shaking, two hours was allowed for the disengagement of the gas, which was then measured.

Warrington's modification.—A graduated shaking-tube is employed;² it allows the nitrate solution and oil of vitriol to be brought to a definite volume. The nitrate solution, with rinsings, is always 2 cc., and enough sulfuric acid is added to increase the volume to 5 cc. The sulfuric acid should give no gas when shaken with distilled water. Any gas given off in the apparatus before shaking is not expelled but is included in the final result. The persistent froth sometimes noticed when some kinds of organic matter are present is reduced by adding a few drops of hot water through the stopcock of the apparatus. The nitric oxide is finally measured. This method, which is accurate for pure nitrates, unfortunately fails in the presence of any considerable quantity of organic matter.

¹ *J. Chem. Soc.*, **21**, 101 (1868).

² *Ibid.*, **35**, 376 (1879).

According to Warington's observations, the presence of chlorides is no hindrance to the accurate determination of both nitric and nitrous acids by the mercury method. This simplifies the operation as carried on by Frankland, who directs that any chlorine present be removed before the determination of the nitric acid is commenced.

Lunge's Improved Apparatus.—Lunge¹ has improved his apparatus for generating and measuring gases and extended its applicability. The part

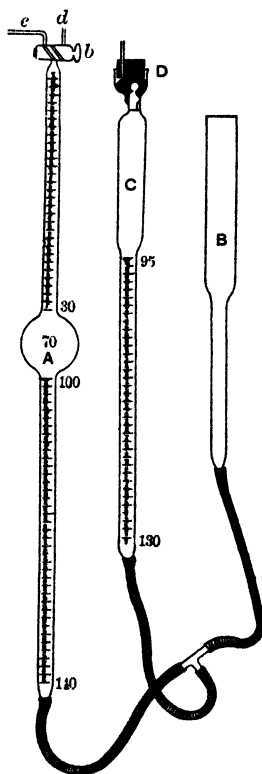


Fig 9 —Lunge's Improved Apparatus

designed to measure the volume of a gas is the same in all cases. For generating the gas, the apparatus varies according to the character of the substance under examination. The measuring apparatus is shown in Fig. 9. It is composed essentially of three tubes, conveniently mounted on a

¹ *Bull. soc. chim.*, **11**, 625 (1894)

wooden holder with a box base for saving any spilled mercury. The support is not shown in the illustration.

The tubes *A*, *B*, *C* are connected by means of a three-way tube and rubber tubing with very thick walls to hold the mercury safely without expansion. In the middle of the measuring tube *A* is a bulb of 70 cc. capacity. Above and below, the bulb is divided into tenths of a cubic centimeter, and its diameter is such, viz. 11.3 millimeters, that each cubic centimeter occupies a length of 1 cc. The upper end of *A* is closed with a glass cock with two oblique perforations by means of which communication can be established at will, either through *c* with the apparatus for generating the gas, or through *d*, with the absorption apparatus, or the opening be completely closed.

Under the observed conditions, the volume of air that would measure exactly 100 cc. at 0° and 760 mm. pressure of mercury is calculated by the formula:

$V = \frac{100 (273 + t) 760}{273 (b - f)}$, where *t* equals observed temperature, *b* the barometric pressure less the correction noted below, and *f* the tension of the vapor of water under existing conditions. For example:

Temperature	18°
Barometric reading	755
Correction for <i>b</i>	2
Corrected barometer	753
Vapor of water tension	16

$$\text{Then } V = \frac{100 (273 + 18) 760}{273 (753 - 16)} = 109.9.$$

This calculation indicates that 109.9 cc of air would occupy a volume of 100 cc when subjected to standard conditions.

The tubes *A*, *B*, and *C* are filled with mercury, of which about 2.5 kg. will be required. By means of the leveling tube *B*, the stopper in *C* being opened, the mercury in *C* is brought exactly to 109.9 cc. The stopper in *C* is then closed, and mercury is poured into *D*, which is then closed with a rubber stopper carrying a small glass tube, as indicated in the figures.

The leveling tube *B* serves to regulate the pressure on the gas in *A*; it is depressed or elevated, as the case may require.

The tube for reducing the volume to standard conditions of temperature and pressure, viz. 0° and 760 mm. of mercury, is shown in *C*. In its narrow part, which has the same internal diameter as *A*, it is graduated to tenths of a cubic centimeter. The upper end of *C* is furnished with a heavy glass neck, *D*, surmounted by a glass cup. In the neck is placed a ground-glass stopper carrying a groove below, which corresponds to a similar groove in the side of the neck, whereby communication can be established at will between the interior of *C*, and the exterior. The joint is also sealed by pouring mercury into *D*, as is shown in the figure. When the stopper is well ground and greased the reduction tube may be raised or lowered as much as may be necessary without any danger of escape or entrance of gas. To determine the position of the reduction tube *C* the reading of the barometer and thermometer at room temperature is taken. From the reading of the barometer

subtract 1 mm. if the temperature is below 12° , 2 mm. at a temperature from 12° to 19° , 3 mm. from 20° to 25° , and 4 mm. above 25° .

When a gas has been introduced into the measuring tube *A* it is brought to the volume which it would assume under standard conditions by adjusting the tube *C* in such a way as to bring the mercury in *C* and *A* to the same height, and the surface of the mercury in *C* is exactly at 100 cc. The gas in *A* is then at the volume which it would occupy under standard conditions, and this volume can be read directly. This adjustment is secured by moving the tubes *B* and *C* up or down. If gases are to be measured wet, a drop of water should be put on the side of the upper part of *C*, and if dry, of sulfuric acid before the adjustment for temperature and pressure.

Method of Manipulation.—By the action of mercury in the presence of sulfuric acid, the nitrogen in nitrates, nitrites, nitrosulfates, nitroses, nitrocellulose, nitroglycerol and the greater number of explosives may be obtained and measured as nitric oxide. The nitrogen compounds are decomposed in the apparatus shown in Fig. 10.

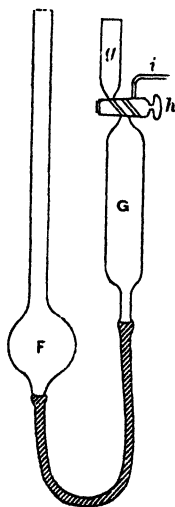


Fig. 10.—Lunge's Decomposition Apparatus.

To make an analysis, the apparatus is filled with mercury, through *F*, until the two openings in the cock and *i* are entirely occupied with that liquid. The cock *h* is then closed, and the nitrogen compound, in solution, is introduced through *g*, care being taken that no air enters *g* when *F* is depressed and *h* is opened to admit the sample. The funnel *g* is washed several times with a few drops of sulfuric acid, which are successively introduced into *G*. The total liquid introduced should not exceed 10-15 cc., of which the greater part should be sulfuric acid. The rubber tube connecting *G* and *F* is carefully closed with a clamp, and *G* is violently shaken for a few minutes, until no further evolution of nitric oxide takes place. In shak-

ing, the apparatus should be so held as to prevent the escape of the mercury from the small tube *i* by keeping it closed with the finger or drawing over it a rubber cap

After the evolution of the gas has ceased, the tube *c* (Fig. 9) is brought into contact with *i* (Fig. 10), and the two are joined by a tight-fitting piece of rubber tubing in such a way as to exclude any particle of air. The tube *F* (Fig. 10) is lifted, and *B* and *C*, Fig. 9, are depressed. On carefully opening the cocks *h* and *b* and bringing *i* and *c* into union, the gas is passed from *G* into *A*. When all the gas has entered *A* and the acid mixture from *G* has reached *b*, the latter is closed, as is also *h*. The apparatus *G* is disconnected and removed. The gas in *A* is then reduced to normal conditions by manipulating the reduction tube *C* in the manner already described.

The gas in *A* is measured dry because it has been generated in the presence of rather strong sulfuric acid. Consequently, for this operation the adjustment of the volume of gas in *C* should be made in contact with a drop of strong sulfuric acid. In order to make the readings, such a quantity of material must be taken as will give not less than 30 and not more than 140 cc. of nitric oxide.

Utility of the Method.—If it is desirable to use the nitric oxide method and at the same time avoid heating, the decomposition of a nitrate by means of metallic mercury and sulfuric acid affords a convenient and accurate procedure. As a rule there is no objection to the application of the lamp except in the case of explosives, and in such cases the mercury method appears to have no advantage over the ferrous chloride process. Nevertheless, in the hands of a skilled worker, the results are reliable, and the process is a quicker one, on the whole, than that by distillation with ferrous chloride and hydrochloric acid.

Du Pont Nitrometer.—The du Pont nitrometer is a modification of Lunge's apparatus. Beckett¹ investigated this nitrometer as applied to the analysis of explosives and concluded that there is an appreciable quantity of nitrogen and nitrous oxide gas left in the sulfuric acid residue after the estimation of nitrogen in du Pont's high nitrogen gun cotton, gun cotton, highly soluble nitrocellulose, blasting soluble nitrocellulose, and sodium nitrate. In conclusion, Beckett stated that the nitrometric estimation of nitrogen in nitrocellulose is invariably too low. He found that the time which is allowed to elapse between the introduction of the nitrocellulose and sulfuric acid into the nitrometer and the shaking has a decided influence on the results, in the case of nitrocellulose, but that this effect is less in the case of inorganic compounds. The results most nearly correct are obtained by using 15 cc. of 92.5-94 per cent sulfuric acid and by allowing 15 minutes to elapse between the introduction of the nitro-

¹ *J. Chem. Soc.*, 117, 220 (1920).

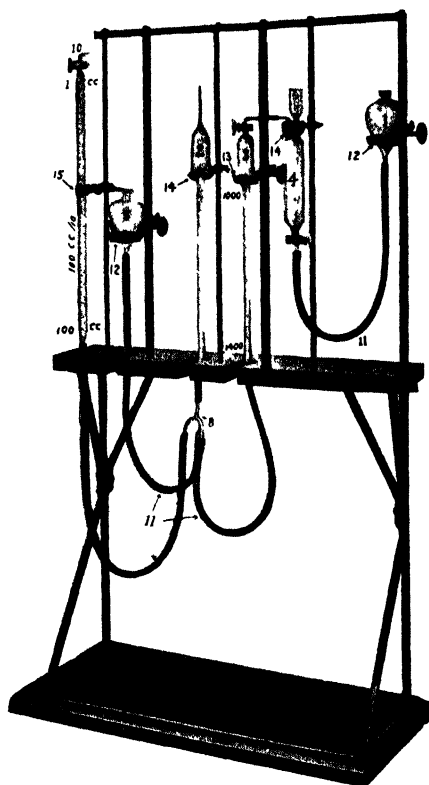


Fig. 11—DuPont Nitrometer

cellulose and acid into the nitrometer and shaking. In this case he stated that the error is approximately 0.7 per cent.

Since the du Pont nitrometer can be used only in the analysis of inorganic nitrates and mixed acids and then only by approximating the true results through the elimination of the errors in the method by standardization with a pure nitrate, and since a better method for fertilizer control appeared to be available, the referee (Phelps)¹ in 1920 recommended that the study of the du Pont nitrometer be abandoned.

Sodium Nitrate by the Method of Difference.—In the analysis of Chile saltpeter by the direct method a variation from the dealers' guaranty of 0.25 per cent in the content of nitrogen is allowed—the equivalent of a total variation in the content of sodium nitrate of 1.52 per cent. Dealers

¹ *J. Assoc. Official Agr. Chem.*, 5, 104 (1921)

and shippers have always been accustomed to estimate the quantity of sodium nitrate in a sample by difference, *i. e.*, by estimating the constituents not sodium nitrate and subtracting the sum of the results from 100. Chile saltpeter usually contains sodium nitrate, water, insoluble ferruginous matters, sodium chloride, sodium sulfate and sometimes small quantities of potassium nitrate.

The method by difference, also termed the West Coast refraction method, as given by Haskins¹ is as follows:

Moisture.—Weigh accurately, approximately 10 grams of the material (60 mesh), spread out on a tared watch-glass and dry in a hot-air oven at 160° C. for exactly 5 hours; cool in a desiccator and weigh. The loss in weight represents moisture.

Insoluble residue.—Dissolve approximately 50 grams of the material in 200-300 cc. of hot water and filter, preferably on a weighed Gooch crucible. Make the filtrate up to 1000 cc. and preserve it for the subsequent determinations of the other impurities. Dry the crucible and contents at 120-130° C. to constant weight. The net weight represents the total insoluble matter.

Sodium chloride.—Titrate 100 cc. of the solution, equivalent to 5 grams of material, with 0.1 N silver nitrate solution. Before beginning the titration add 1-2 mg. of sodium carbonate to sharpen the end point with the potassium chromate indicator (1 cc. of a saturated potassium chromate solution). Add the silver nitrate solution slowly so that the red precipitate of silver chromate disappears as fast as it is formed; otherwise there is a danger of its being occluded in the silver chloride. Take the end point at the first permanent reddish tint. One cc. of 0.1 N silver nitrate equals 0.005846 gram of sodium chloride. Report as "Total chloride equivalent to — per cent of NaCl."

Sodium sulfate.—In the determination of sulfates use exactly 100 cc. of the filtrate from the insoluble residue determination. Expel nitric acid by evaporation with an excess of hydrochloric acid. Precipitate the sulfuric acid with 10 cc. of 10 per cent barium chloride solution. Barium sulfate $\times 0.60859$ = sodium sulfate. Report results in terms of sodium sulfate.

Potash.—Determine the percentage of potassium oxide according to the official method.

This method might give correct results if the sample contained only the materials mentioned, but other compounds may be present, such as sodium carbonate, potassium nitrate, sodium chlorate, sodium perchlorate, and salts of iron, alumina, lime and magnesia. The various determinations and calculations involved in this method take approximately three times as much time as is required by the direct estimation of nitric nitrogen. When the determinations outlined above have been carefully made, it is claimed that the result obtained by subtraction from 100 will not vary

¹ *J. Assoc. Official Agr. Chem.*, **4**, 66 (1920).

more than 0.2-0.3 per cent from the true content of sodium nitrate. The method, however, cannot be considered strictly scientific, and it is much more tedious than the direct determination of nitrogen. If potassium is present in appreciable quantities, the percentage of sodium nitrate calculated from the percentage of nitrogen will be too low, but as the material is sold on the basis of its content of nitrogen, this is of little practical importance.

ESTIMATION OF NITRIC ACID BY OXIDATION OF A COLORED SOLUTION

Solutions of organic coloring matter in certain conditions are decolorized by nitric acid. The process is one of oxidation and the disappearance of the natural color marks the end of the reaction. Indigo is the only coloring matter that has been used to any extent in this process.

Marx Method.—The indigo method is usually conducted according to the principle described by Marx.¹ The following reagents and apparatus are required:

REAGENTS

- (a) A solution of pure potassium nitrate containing 1.8724 grams per liter; 1 cc. of the solution is equivalent to 1 mg. of nitric anhydride (N_2O_5).
- (b) A solution of the best carmine in water, approximately standardized by solution in the manner described hereafter, and then diluted so that 6-8 cc. is equivalent to 1 mg. of nitric acid.
- (c) Chemically pure sulfuric acid, sp. gr. 1.842, perfectly free from sulfurous and arsenious acids and nitrogen oxides.
- (d) Several thin flasks of about 200 cc. capacity.
- (e) A small cylindrical measure holding 50 cc. and divided into cubic centimeters.
- (f) A Mohr buret divided into tenths of a cubic centimeter.
- (g) A 25 cc. pipet or another buret.
- (h) A 5 cc. pipet divided into cubic centimeters or half cubic centimeters.
- (i) A measuring flask of 250 cc. capacity.

PRELIMINARY TRIAL

Transfer 25 cc. of the sample to a flask, fill the 50 cc. measure with sulfuric acid and fill the buret with indigo solution. Add all the sulfuric acid to the sample at one time, shake for a moment, and then run the indigo in as quickly as possible, shaking until a permanent greenish tint is produced. If the sample does not require more than 20 cc. of indigo solution of the above strength, titrate directly; otherwise dilute with a proper quantity of pure water and resubject to the preliminary trial.

¹ *Z. anal. Chem.*, **7**, 412 (1868).

ACTUAL TITRATION

(1) Pour 25 cc. of the sample, properly diluted if necessary, into a flask and add as much indigo as was used in the preliminary trial. Add all at once, a quantity of sulfuric acid equal in volume to the liquid in the flask, shake the mixture, and then quickly add indigo solution out of the buret until the liquid remains permanently of a greenish tint. (2) Repeat the last experiment as often as may be necessary, adding to the water at first 0.5 cc. less indigo than the total quantity used previously, afterwards proceeding as in (1) until the final test shows too little indigo used. (3) From the rough titration of the indigo, calculate the quantity of potassium nitrate solution corresponding to the indigo solution used in (2), multiply the result by 10, transfer this quantity of the standard nitrate solution to a 250 cc. flask, fill with pure water to the mark, and titrate 25 cc. of this fluid with indigo as in (2). If the quantity of indigo solution is nearly the same as that required in (2), calculate its exact value, but if it is not, make up another nitrate solution in the 250 cc. flask that more closely resembles the sample in strength, and repeat the titration with the indigo solution. (4) If the water contains any considerable amount of organic matter, first destroy it by potassium permanganate. In this case, the estimation of the organic matter and nitric acid may be conveniently combined. The use of permanganate is likely to introduce an error, as has been shown by Warington. The method, therefore, cannot be recommended in the presence of organic matter.

Calcium Nitrate.—The analysis of calcium nitrate presents difficulties owing to the extremely hygroscopic nature of the salt, which renders it impossible to weigh the portion required for analysis in the usual way. The material should be crushed quickly in a dry mortar, mixed with a spatula, and transferred to a sample bottle stoppered with a rubber stopper. A quantity may be placed in a glass-stoppered weighing bottle, weighed and about 15 grams poured into a beaker. The bottle is weighed again. Another method is to weigh the bottle first, transfer about 11 grams of the sample to it, and weigh again. The sample is dissolved and made up to 1000 cc. in a graduated flask.

McCandless and Burton¹ recommend that 20 cc. be evaporated to complete dryness in a Kjeldahl flask, with the addition of about 0.4 gram of sodium carbonate. Nitrogen is then estimated in the dried residue by the salicylic-sulfuric acid method. Since commercial calcium nitrate contains ammonium nitrate, and the ammonia is driven off in the above process, it is necessary to estimate the ammonia in another aliquot of 25 cc. in the usual way by distillation with caustic soda. The nitrogen so obtained is added to the nitrogen found in the nitrate. This method requires two determinations. It should be possible to estimate the nitrogen directly in a 25 cc. aliquot by means of the Devarda method.

¹ *J. Assoc. Official Agr. Chem.*, **10**, 216 (1927).

Nitron Method.—The base nitron forms a difficultly soluble crystalline nitrate which can be used for the estimation¹ of nitric nitrogen when the quantity is not too small, as follows:

Dissolve 10 grams of the nitrate (or salt containing about 0.1 gram of nitric nitrogen) in 500 cc. of distilled water and pipet 25 cc. into a 200 cc. beaker. Dilute with 100 cc. of water, add 10 drops of dilute sulfuric acid, and heat almost to boiling. Add 10 cc. of nitron acetate solution and cover, then place the beaker in ice water for an hour. Filter through a weighed Gooch crucible, wash with ice water, and dry at 100 cc. to constant weight. The weight of nitron nitrate ($C_{20}H_{18}N_4 \cdot HNO_3$), multiplied by 0.03733, gives the weight of nitric nitrogen. Make the solution of nitron acetate by dissolving 10 grams of nitron in 100 cc. of water and 5 cc. of acetic acid and keep in a dark bottle to protect it from the light.

Nitron is diphenyl-endo-anilo-hydro-triozal, and approximately 0.0009 gram of the nitrate is soluble in 100 cc. of water. Bromides, iodides, nitrous acid, chromic acid, chloric acid, perchloric acid, picric acid and oxalic acid interfere with the determination.

Prince² tested the nitron method in 1927 and found it accurate and comparatively simple even in the presence of cyanide and urea. The high cost of nitron, however, eliminates the method for use in routine or control work, though it could be used for check work or for special purposes.

ESTIMATION OF FORMS OF COMBINATION OF NITROGEN IN MIXTURES

A difficult problem that is still under investigation is the estimation of the nitrogen in each form of combination in which it exists in a mixture. Methods that are suitable for a single form of combination may not be suitable for mixtures, because the reagents may act upon other constituents besides the one to be estimated.

Qualitative Examination.—*Ammonia.*—Some of the sample is mixed with a little powdered soda-lime. If ammoniacal nitrogen is present, free ammonia is evolved even in the cold and may be detected either by its odor or by testing the escaping gas with litmus or turmeric paper. A glass rod moistened with strong hydrochloric acid will produce white fumes of ammonium chloride when brought near the escaping ammonia.

Nitrates in notable amounts are diluted by treating an aqueous solution of the sample with a crystal of ferrous sulfate and strong sulfuric acid. The iron salt should be placed in a test tube with a few drops of the solu-

¹ Scott, *Standard Methods of Chemical Analysis*, 4th ed., 1925, p. 345.

² *J. Assoc. Official Agr. Chem.*, **11**, 186 (1928).

tion of the fertilizer, and the sulfuric acid should be poured down the sides of the tube in such a way as to run under and not to mix with the other liquid. The tube must be kept cold. A dark brown ring will mark the disk of separation between the sulfuric acid and the aqueous solution in case nitrates are present in appreciable amounts. If the water solution of the sample is too highly colored, the sample may be dissolved in alcohol of 80 per cent strength. The coloration produced when alcohol is used is of a rose or purple tint.

Nitric nitrogen may also be detected by means of brucine. If a few drops of an aqueous solution of brucine are mixed with the same quantity of an aqueous extract of the sample under examination and strong sulfuric acid is added, as described above, a persistent tint varying from rose to yellow will develop at the disk of contact between the acid and the mixed solutions.

The nature of the organic substances containing nitrogen is often revealed by simple inspection, as in the case of cottonseed meal. Frequently, however, the microscope must be used to determine the carrier of the organic nitrogen. The presence of hair, horn, hoof, dried blood, tankage, etc., may frequently be ascertained by microscopic examination, but detailed methods cannot be described here. In most cases the qualitative chemical and microscopic examination will be sufficient. There may be cases, however, where the analyst will be under the necessity of using other means of identification suggested by his skill and experience or by the circumstances. Then the general appearance, odor, and consistency of the sample may afford valuable indications which will aid in discovering the origin of the nitrogenous materials.

Differences in the density of various materials may be used to some extent in their separation. If the material is mixed with chloroform or carbon tetrachloride, heavy particles will sink and the lighter material will rise to the surface, permitting a certain degree of separation, especially if the material is coarsely ground, or not moist. Subsequent microscopic or physical examination of the separates may result in their identification.

Ammonia in Mixtures.—The method for estimating ammonia in mixtures consists in distilling the solution with magnesium oxide, as already described. If, however, the material contains urea, the results are likely to be too high, as urea is decomposed in hot solutions by magnesium oxide, with the formation of ammonia. Ammonia may be estimated in the presence of urea if the ammonia is removed by aeration instead of distillation. The following method may be used:

Prepare an apparatus consisting of a 400 cc. Erlenmeyer flask fitted with a three-hole rubber stopper. Run a tube through one perforation to the bottom of the flask and connect with wash bottles, one of which contains a solution of caustic soda and another dilute sulfuric acid to purify the air. The second perforation carries a dropping funnel, and the third has a tube leading into the receiving flask containing standard acid. This flask has a two-hole rubber stopper, one hole taking the tube from the decomposition flask, and the other connecting with suction. Extract 7 or 10 grams of the fertilizer with distilled water and make up to 500 cc. Place 50 cc. in the Erlenmeyer flask. Add 50 cc. of caustic soda of about 45° Bé. through the dropping funnel. Suck a current of air purified by the caustic soda solution and sulfuric acid solutions through the apparatus for 2 hours, keeping the temperature of the liquid 10-15° C. Titrate the standard acid as usual.

Jones Method for Nitrates and Ammonia.—The Jones method,¹ proposed for the estimation of nitrates, reduces the nitrates with iron and provides a blank determination to correct for the action of the sodium hydroxide upon the urea or other organic material. The method is described as follows:

Test the fertilizer qualitatively for nitrates. If present, proceed as follows:

(1) *Preparation of Solution.*—Place 4 grams of the sample in a 150 cc. beaker, add 40 cc. of water, stir, filter by decantation into a 200 cc. graduated flask, and after all the residue is transferred to the filter wash to just under the 200 cc. mark, letting each washing run through before another is added. Make to 200 cc., mix, and treat aliquots of 50 cc. each as directed below.

Or, place 4 grams of the sample in a 200 cc. flask, add 160 cc. of water, shake thoroughly for 5 minutes, make to 200 cc. in a graduated flask, and filter.

(2) *Ammoniacal Nitrogen.*—Place 50 cc. (equivalent to 1 gram) of the solution prepared according to (1) in a 500-600 cc. Kjeldahl distillation flask and add 150 cc. of water and 5 grams of magnesium oxide (heavy). Connect with a condenser, distil 100 cc. of the liquid into a measured quantity of standard acid, and titrate with standard alkali, using cochineal or methyl red indicator.

(3) *Nitrate Nitrogen.*—Take aliquots for A and B from the same solution and run at the same time. (A) Place 50 cc. of the sample prepared according to (1) in a 500-600 cc. Kjeldahl distillation flask, add 10 to 12 perforated glass beads (3-5 mm.), 2 grams of reduced iron, and 10 cc. of dilute sulfuric acid (1 + 1). Rotate slowly and when violence of reaction has moderated, if any, place on a hot plate and boil gently for 5 minutes. Remove, add 40 cc. of water, and cool. Add 100 cc. of strong sodium hydroxide solution, about 42° Bé. (555 grams of sodium hydroxide in 1 liter of water). Connect at once with an upright condenser by means of a Kjeldahl connecting bulb, and boil until 150-160 cc. has distilled over, and the distillate, as it drops from the condenser, shows neutral to litmus paper. Collect the ammonia in a measured quantity of standard acid and titrate with a standard alkali, using cochineal or methyl red indicator.

¹ *Ind. Eng. Chem.*, **19**, 267 (1927); *J. Assoc. Official Agr. Chem.*, **11**, 32 (1928).

(The nitrogen obtained represents that from nitrates, ammonia salts, and other nitrogenous compounds, proteins, cyanamide, urea, etc., that have been changed, wholly or partially, to ammonia by this treatment.)

(B) *Correction Blank*.—Place 50 cc. of the sample prepared according to (1) in a 500-600 cc. Kjeldahl distillation flask and proceed exactly as under (A), but do not add reduced iron.

The nitrogen obtained represents that from ammonia salts and other nitrogenous compounds, proteins, cyanamide, urea, etc., that have been changed wholly or partially to ammonia by this treatment.

The percentage of nitrogen obtained by procedure (A) minus that obtained by procedure (B) equals the percentage of nitrogen from nitrates contained in the sample.

CAUTION: When cyanamide is present in amounts greater than 150 pounds per ton or the distillate under (3-A) or (B) fails to show neutral when finally tested with litmus paper, repeat procedures (A) and (B), using a 25 cc. aliquot (0.5 gram) and add 25 cc. of water previous to the addition of the 10 cc. of sulfuric acid ($1 + 1$).

General Observations on the Jones Method.—A critical study of this method indicates that its success depends on securing a proper blank for correction (B). This, it is evident, must very closely offset any change due to the evolution of hydrogen other than its action on the nitrate present. For this reason the concentrated soda solution was employed.

The addition of perforated glass beads insures gentle boiling, free from bumping, and no frothing. From 50 to 60 minutes is usually required for the distillation of (A) and (B), and the flasks should rest on asbestos-coated wire gauze. At the completion of the process add water to the flasks before cooling to prevent caking. In making the solution of the sample it is only necessary to dissolve all the nitrate and ammoniacal salts present. The amount of nitrogen from tankage, cyanamide, etc., that remains undissolved is unimportant.

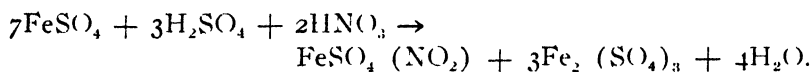
The experiments of Jones with the proposed method indicate that any action of hydrogen on the organic materials is offset by the effect of the concentrated soda solution used in the blank. The apparent nitrate present was 0.03-0.11 per cent in the samples containing cyanamide with no nitrate; in other samples the blank was greater than the determination but within the limits of error.

The official reduced iron method, in the samples containing cyanamide, indicated 0.56, 1.12, and 1.65 per cent of nitrate nitrogen though none was present.

It seems possible that cyanamide or urea added to superphosphate may be partially converted to ammonia. This portion is now classed as mineral nitrogen regardless of its original source.

Robertson Method.¹—The methods used at the present time for distinguishing sharply between the organic and mineral nitrogen when cyanamide, urea and acid fish are used in fertilizer mixtures are not entirely satisfactory. The Arnd, Devarda and reduced iron methods are known to give erroneous results in the presence of such materials. While the Jones method is a distinct improvement over these methods for the determination of mineral nitrogen in commercial fertilizers in the presence of calcium cyanamide and urea, it is not so rapid, accurate or definite. A method suggested by B. F. Robertson at the 1927 meeting of the A. O. A. C., involving the following principle was tried out by the Referee on Nitrogen during 1928 and 1929.

An aliquot portion of the fertilizer solution is boiled with sulfuric acid and ferrous sulfate. In the reaction of the nitrates the nitrogen monoxide (NO) produced combines with the ferrous sulfate to form an unstable compound.



During the digestion, the nitrate nitrogen is thereby driven off. The water-soluble nitrogen is previously determined by subtracting the insoluble nitrogen from the total nitrogen. Then the difference between the water-soluble nitrogen and the nitrogen obtained after the ferrous sulfate digestion gives theoretically the nitrate nitrogen. The actual procedure is as follows:

- (1) Determine the total nitrogen by the usual method.
- (2) Weigh out 2 grams of the fertilizer mixture, wash to 200 cc., and determine the nitrogen in the residue by any of the modifications of the Kjeldahl methods. The difference between the results of these two determinations gives the water-soluble nitrogen.
- (3) Distil 50 cc. of the filtrate, equivalent to 0.5 gram, with magnesium oxide for ammoniacal nitrogen as described in *Methods of Analysis*, A. O. A. C.
- (4) Take another 50 cc. portion of the same solution, put into a 500 cc. Kjeldahl flask together with 2 grams of ferrous sulfate and 20 cc. of sulfuric acid (sp. gr. 1.84). Digest over a hot flame. After the water is evaporated and white fumes appear, continue the digestion for at least 10 minutes, thereby driving off the nitrate nitrogen. If the solution does not clear, add 0.65 gram of mercury and boil until clear, dilute, and add potassium sulfide solution to precipitate mercury as usual. Cool, dilute, and distil with strong caustic soda in the usual way. Add a pinch of a mixture of zinc dust and granular zinc (20 mesh) to each flask before distillation to prevent bumping.

¹ *J. Assoc. Official Agr. Chem.*, **12**, 176 (1929).

1 (total)—2 (water-insoluble) gives water-soluble nitrogen. The difference between the water-soluble nitrogen and the nitrogen obtained in 4 gives the nitrate nitrogen. 3 (ammonia nitrogen) + nitrate nitrogen gives total mineral nitrogen. Total nitrogen less mineral nitrogen gives the organic nitrogen.

This method is being studied by the A. O. A. C., and the latest revision of the methods should be consulted.

Short Robertson Method for Nitrates.—When water-soluble nitrogen is not desired, the use of ferrous sulfate offers a short method for the determination of nitrates alone. To 0.5 gram in a Kjeldahl flask add 50 cc. of water and 20 cc. of concentrated sulfuric acid. Digest until the water is evaporated and white fumes appear. Add 0.7 gram of mercury and complete the work as usual. Subtract the nitrogen so secured from the total nitrogen to get the nitric nitrogen. This method was suggested by Jones in 1929.

Nitrogenous Chemicals in Animal or Vegetable Nitrogenous Materials.—Moore and White¹ studied methods for estimating any nitrogenous adulterants that may be added to tankage. The methods could be useful for this purpose as well as for others.

Mechanical Separation of Cyanamide and Sulfate of Ammonia.—The silver nitrate test for cyanamide usually fails to show this material when present in tankage. If some of the sample is mixed with carbon tetrachloride, the heavy particles, including cyanamide, sulfate of ammonia, etc., will settle to the bottom of the container, while the tankage will float. Cyanamide can easily be detected in the portion which settles, by means of silver nitrate. The test should be applied as follows:

Place 30-40 grams of the tankage, preferably ground to pass a 10-mesh sieve, in a beaker, add about 200 cc. of carbon tetrachloride, and stir. After allowing the mixture to settle a short time, transfer the lighter floating material, along with most of the carbon tetrachloride, to another container and test the heavier portion for sulfate of ammonia, cyanamide, etc. If the carbon tetrachloride-tankage mixture is mixed with an approximately equal volume of turpentine, crystals of urea, if present, will appear floating or in partial suspension.

Qualitative Tests for Sulfate of Ammonia, Urea and Cyanamide.—Mix about 5 grams of the sample with about 150 cc. of water in a beaker. After allowing to stand for a few minutes, filter and test the filtrate as described below. For nitrates, use the test for ferrous sulfate already described.

Cyanamide.—Dry a small portion of that part of the sample which settled out when mixed with carbon tetrachloride, stir with water and

¹ *Ind. Eng. Chem.*, **19**, 264 (1927).

filter. To a portion of this filtrate add 10 cc. of 5 per cent solution of silver nitrate. A yellow or brownish yellow precipitate indicates cyanamide. This cyanamide precipitate is insoluble in ammonia, but soluble in nitric acid. There is little difficulty, however, in detecting cyanamide, as the characteristic odor is evident in that portion which settles from carbon tetrachloride.

Sulfate of Ammonia.—The needle-like crystals of sulfate of ammonia are usually detected by the naked eye or with the aid of a magnifying glass. Its presence can be confirmed by adding a few drops of caustic soda to a portion of the same filtrate mentioned and warming slightly. Ammonia fumes will indicate the presence of ammonia salts. Another portion of the filtrate can be tested with barium chloride. A precipitate of barium sulfate will be formed if sulfates are present.

Urea.—Test a portion of the filtrate by adding a few drops of bromine water and caustic soda solution. If urea is present, the solution will effervesce, liberating nitrogen gas. Urea melts at about 132° C., losing ammonia and forming biuret, which when treated with a solution of caustic soda containing a trace of copper sulfate produces a reddish violet solution.

QUANTITATIVE DETERMINATION

Solution 1.—Transfer 5 grams of the ground tankage to a beaker, and add about 100 cc. of grain or denatured alcohol (formula No. 30) redistilled over caustic soda until practically anhydrous. Allow to stand 30 minutes, stirring frequently. Transfer the residue from the beaker to a filter and wash with alcohol, finally making the volume of the filtrate to 250 cc.

Solution 2.—Wash the residue on the paper from Solution 1 into a 250 cc. volumetric flask with about 150 cc. of water, shake frequently for 15-30 minutes finally making to volume. Pass through a dry filter and use the filtrate for determining ammoniacal nitrogen.

Solution 3.—Transfer 5 grams of the sample into a 250 cc. volumetric flask, add about 200 cc. of water, stopper, and shake frequently for 1 hour. Make to volume and pass through a dry filter. Use this solution for determining cyanamide and nitrate nitrogen.

Nitrogen in Form of Nitrate.—Transfer two 50 cc. portions of Solution 3 to separate Kjeldahl flasks and determine nitrate by the Jones method, previously described.

Nitrogen in Form of Cyanamide.—To a 50 cc. aliquot of Solution 3 add an excess of 5 per cent silver nitrate solution, and finally 20 cc. of 10 per cent potassium hydroxide solution. Filter and wash the brown precipitate and determine nitrogen in the residue by the Kjeldahl method, substituting 1 gram of copper sulfate in place of mercury (modified Caro method). (This method includes nitrogen present as cyanamide and as dicyandiamide.)

Nitrogen as Ammonium Sulfate or Ammonia Salts.—Transfer a 50 cc. aliquot from Solution 2 to a Kjeldahl flask, add 150 cc. of water and excess of magnesium oxide, and distil. The ammonia thus collected indicates that present in the form of ammonia salts, usually referred to as free ammonia. If urea is not present, use Solution 3, but extraction with alcohol will remove small quantities of urea usually present in organic materials.

Nitrogen as Urea.—Transfer 50 cc. of the alcoholic solution into a 500-600 cc. Kjeldahl flask, add 100 cc. of water, and cool. Add 0.25 gram of urease, connect the flask to the condenser, and allow to stand cold for 30 minutes, shaking frequently. Finally add about 1 gram of paraffin and 5 grams of heavy magnesium oxide, and distil until about 100 cc. has been collected. The nitrogen present in the urea is converted by the urease quantitatively to the form of ammonia, which is distilled and collected as described previously in excess standard acid. If ammonium nitrate, which is slightly soluble in alcohol, is present, this procedure should be slightly modified as follows: Transfer 50 cc. of Solution 1 into a 500-600 cc. Kjeldahl flask, add 75 cc. of nearly absolute alcohol, add magnesium oxide, and distil about 75 cc., collecting in standard acid. The ammonia thus collected would otherwise be determined as urea ammonia. This recovered ammonia should be added to the free ammonia as determined in Solution 2.

When the free ammonia is determined by distillation with magnesium oxide, without removing urea, too much ammonia is found. It is thus apparent that when urea is present it is necessary to remove it with alcohol in order to determine the free ammonia accurately, as from 5 to 10 per cent of the ammonia in urea will be driven over by boiling with magnesium oxide and water.

The modified Caro method for determining cyanamide ammonia gives slightly high results. It is advisable, when cyanamide is present, to make up a mixture of known analysis to run along as a check.

ESTIMATION OF NITROGENOUS CONSTITUENTS OF CALCIUM CYANAMIDE

The methods for the estimation of the nitrogenous constituents of calcium cyanamide, as furnished by the President of the American Cyanamid Company, are given below. These methods may be useful in other connections. In alkaline solution, cyanamide tends to change to other forms of nitrogen compounds. It is necessary, therefore, not to permit alkaline cyanamide solutions on which determinations are to be made, to stand longer than a few minutes. In the procedure below, cyanamide and urea are determined from one solution. Dicyandiamide and guanylurea are determined from separately weighed samples. In the determination of cyanamide and urea, it is advisable to carry the cyanamide determination

through the precipitation of the silver cyanamide and to carry the urea determination through the point where the urease addition is made. The cyanamide determination may then be completed during the progress of the urea determination.

Total Nitrogen.—Weigh a 1 gram sample into a Kjeldahl flask, add 30 cc. of concentrated sulfuric acid, and heat for 1 hour on the rack. Complete the determination according to the regular Kjeldahl procedure, using 0.5 N acid.

Cyanamide Nitrogen.—Weigh a 5 gram sample into a porcelain mortar and grind thoroughly with water. Transfer the mixture to a 500 cc. volumetric flask and shake at short intervals for 30 minutes. Filter the solution through a dry paper, rejecting the first 25 cc. of filtrate. Pipet a 50 cc. portion into a 600 cc. beaker, dilute to 300 cc., and add 5 cc. of concentrated ammonia and an excess of 5 per cent silver nitrate solution. Stir to coagulate the precipitate, filter, and test the filtrate for complete precipitation by adding more silver nitrate solution. Wash the precipitate with cold water until the washings are no longer alkaline to phenolphthalein. Transfer the filter paper and precipitate to a Kjeldahl flask and determine the nitrogen by the regular Kjeldahl procedure, using 0.1 N standard acid and alkali solutions. Report the result as percentage of cyanamide nitrogen.

Dicyandiamide Nitrogen.—Grind a 2 gram sample with water in a porcelain mortar for 30 minutes. Filter into a 100 cc. volumetric flask. Wash the residue until the volume of the filtrate is nearly 100 cc. Make the solution neutral to phenolphthalein and make the volume up to 100 cc. Pipet a 25 cc. portion into a 150 cc. beaker and add exactly 7 cc. of concentrated hydrochloric acid. Suspend the beaker over a gently boiling water bath and leave it there exactly 15 minutes. Allow the solution to cool and then add 40 per cent sodium hydroxide until the solution is just barely alkaline to phenolphthalein. Add 5 cc. of alcoholic picric acid solution (6 grams in 100 cc. of 95 per cent alcohol). Allow to stand for 1 hour, filter on a weighed Gooch crucible, and wash with a little cold water. Dry at 105° C., cool in a desiccator, and weigh. Add a correction of 0.0044 gram for each 25 cc. of filtrate and washings. Multiply the corrected weight of the precipitate by 0.169 to obtain dicyandiamide nitrogen. Correct for any guanylurea present in the original sample and report as percentage of dicyandiamide nitrogen. This determination depends upon the hydrolysis of dicyandiamide to guanylurea and the precipitation as guanylurea picrate.

Urea.—Pipet a 50 cc. portion of the solution for the determination of cyanamide into a 600 cc. beaker, dilute to 400 cc., and make exactly neutral to methyl red. Add a solution of 0.5 gram of urease in 25 cc. of water that has been made neutral to methyl red. Allow the solution to stand overnight at room temperature or for 3 hours at about 40° C. Add a few drops of methyl red if necessary and a measured excess of 0.1 N hydrochloric acid. Remove carbon dioxide by aerating with purified air and titrate with 0.1 N sodium hydroxide solution.

If more than 10 cc. of 0.1 N acid is neutralized by the ammonia from the urea, the result is not reliable and the determination should be repeated with a smaller sample. The urease method is based upon the fact that in approximately neutral solution, urea is quantitatively converted to ammonium carbonate by the enzyme urease, which occurs principally in the soy or jack bean. So far as is known the

urease method is specific for urea. Cyanamide, dicyandiamide and guanylurea have no influence. In the presence of calcium salts the calcium must be removed by the use of sodium carbonate and the excess of carbonate destroyed by acidification and aeration before the urease is added. In the analysis of the fertilizer mixtures containing soluble phosphates, the phosphate must be removed with barium hydroxide and the excess of barium with sodium carbonate. The excess of sodium carbonate is then removed by acidification.

Guanylurea.—Weigh a 2 gram sample into a mortar and grind with water for half an hour. Filter into a 100 cc. volumetric flask and wash the residue until the volume of the filtrate is nearly 100 cc. Make the solution exactly neutral to phenolphthalein by adding dilute nitric acid (1 + 3). Make up to 100 cc. and pipet a 25 cc. portion into a 150 cc. beaker. Add 5 cc. of alcoholic picric acid solution and scratch the sides of the beaker for 2 minutes. Allow to stand for at least 1 hour. Filter the precipitate of guanylurea picrate on a weighed Gooch crucible. Wash any precipitate remaining in the beaker into the crucible, using two portions of 5 cc. each of distilled water. Dry the precipitate at 105° C. for 1 hour, cool in a desiccator, and weigh. Add a correction of 0.0041 gram for each 25 cc. of filtrate and washings. Multiply the correct weight of the precipitate by 0.169 to obtain guanylurea nitrogen.

Insoluble Nitrogen.—Weigh a 2 gram sample into a mortar and grind thoroughly with water. Filter on a paper and wash the residue with at least 250 cc. of water. Transfer the paper to a Kjeldahl flask and determine the nitrogen in the residue by the usual Kjeldahl procedure.

UREA ALONE AND IN PRESENCE OF CYANAMIDE

A study of the estimation of urea alone and in cyanamide has been made by Fox and Gelderd.¹ The method is based upon the conversion of urea into ammonium carbonate by the enzyme urease and the estimation of the ammonia so formed by means of standard acid.

In aqueous solutions the enzyme urease converts urea into ammonium carbonate and so far as is known it is specific for urea. The ammonia thus formed can then be readily determined by titration with an acid. The enzyme was discovered in the soy bean by Takeuchi about 1909, and has since been found in quite a variety of beans. It occurs principally, however, in the jack bean (*Canavalia ensiformis*). According to Mateer and Marshall, the jack bean contains fifteen times and the sword bean five times as much urease as the soy bean. The enzyme is extremely sensitive to acids and alkalis. Hydrochloric acid in concentrations greater than 0.005 *N* completely inhibits its action, while sodium hydroxide in concentrations greater than 0.02 *N* also inhibits its action. Temperature greatly affects its rate of reaction, each 10° rise in temperature between

¹ *Ind. Eng. Chem.*, **15**, 743 (1923).

10° and 50° C. causing the velocity to nearly double. A temperature of 80° C. or more will destroy its activity.

Most salts have a depressing effect on the action of the urease. Sodium chloride in concentration of 0.25 per cent depresses the rate of reaction to about two-thirds normal, while a concentration of 1 per cent depresses the rate to one-half normal. Barium and calcium chlorides completely inhibit the action of urease after the conversion is about 75 per cent complete. If these salts are present, it is necessary to remove them from solution previous to the addition of the urease. This is readily accomplished by precipitating them as carbonates. The excess carbon dioxide is then removed by aeration.

Several methods of preparing and preserving the enzyme have been devised. The enzyme is more active, however, when freshly extracted, and for that reason it is best to prepare it each day as needed. A few grams of jack-bean flour are extracted with twenty times its weight of water for 10-15 minutes, exactly neutralized with hydrochloric acid (about 1 cc. of 0.1 *N* HCl per gram of jack-bean flour), and filtered. Ten cubic centimeters of this extract is sufficient to convert 0.1 gram of urea to ammonia in less than 1 hour.

Urea in Absence of Interfering Substances.—Weigh out a 0.5 gram sample and dissolve it in 250 cc. of water. Pipet 25 cc. into a tall-form, wide-mouth bottle of about 100 cc. capacity, add a few drops of methyl red indicator and bring to exact neutrality, using 0.1 *N* hydrochloric acid or sodium hydroxide. Add 10 cc. of neutral urease solution and let stand for 1 hour, keeping the bottle stopped. Add from a buret a measured excess of standard 0.1 *N* hydrochloric acid solution, insert into the bottle a glass tube with a small bulb and fine holes at its lower end, connect with the air line through a series of acid and alkali gas-washing bottles, and aerate as vigorously as possible without danger of losing some of the solution through spattering, until all the carbon dioxide is removed (5-10 minutes). Two or three drops of caprylic alcohol or liquid petrolatum added to the solution will prevent frothing. After aerating reduce the current of air and titrate the solution to exact neutrality with 0.1 *N* sodium hydroxide solution. The quantity of nitrogen in the urea is calculated from the 0.1 *N* hydrochloric acid used by the ammonia produced.

Urea in Cyanamide.—Extract 2 grams of cyanamide with 400 cc. of water for 2 hours, add 2 grams of anhydrous sodium carbonate to precipitate the calcium, and continue to shake for another half hour. Filter the extract through a dry filter and take 25 cc. aliquots for the estimation of urea. Pipet the aliquots into the bottles mentioned previously, make the solution distinctly acid with dilute hydrochloric acid, and aerate until all the carbon dioxide is expelled, as shown by the sharpness of the end point in the subsequent neutralization. Then make the solution exactly neutral, using methyl red as indicator, add urease solution, and determine urea as described above.

Nitrates in Presence of Cyanamide or Urea.—Jacob¹ made a study of the estimation of nitrogen by the Devarda method in the presence of cyanamide and urea and proposed the following methods.

1. *Nitrate Nitrogen in Absence of Interfering Compounds.*—This method is essentially that devised by Allen.

Measure a suitable aliquot of the solution containing the nitrate into an 800 cc. Kjeldahl flask, add 5 cc. of 20 per cent sodium hydroxide, and make the total volume up to 350 cc. Connect the flask to a distilling apparatus, fitted with an efficient type of scrubber bulb, and boil until 300 cc. of distillate collects in the receiver which removes all ammonia, either free or combined. Add to the 50 cc. of solution remaining in the flask 200 cc. of water and 1.5-2 grams of nitrogen-free Devarda's alloy (about 60 mesh). Immediately connect the flask with the distilling apparatus, and redistil 200 cc. into a known quantity of 0.1 or 0.05 *N* sulfuric acid in the course of about 1 hour.

The nitrogen, as ammonia, found by titrating the excess sulfuric acid represents the nitrate present in the original aliquot. The Kjeldahl flasks should be free from all traces of Devarda's alloy or zinc before distilling off the original ammonia; otherwise some of the nitrate may be reduced and thus fail to appear in the final nitrate determination.

2. *Nitrate Nitrogen in Presence of Cyanamide, Dicyandiamide and Guanlylurea.*—To a measured sample containing these forms of nitrogen add 100 cc. of a saturated solution of silver sulfate and 10 cc. of a 15 per cent solution of potassium hydroxide. Allow the precipitate to stand for about 1 hour, with frequent stirring, and then filter directly into an 800 cc. Kjeldahl flask; wash the precipitate six times with 10 cc. portions of water, add 5 cc. of 20 per cent sodium hydroxide to the flask, and make the total volume up to about 350 cc. After distilling off the ammonia, determine the nitrate as described above. Urea is only partly removed by this procedure. Run blank determinations on all samples of silver sulfate, as this compound, unless especially purified, usually contains an appreciable quantity of nitrate.

3. *Nitrate Nitrogen in Presence of Urea.*—Treat a neutral aliquot of the original solution containing urea, nitrate, and other forms of nitrogen with 10 cc. of a neutral 2 per cent extract of jack-bean flour and allow to stand for 1 hour. At the end of this time the enzyme urease will have converted the urea present into carbon dioxide and ammonia. In order to free the solution of the nitrogen added in the jack-bean extract, treat with silver sulfate and potassium hydroxide solutions as in the previous procedure, and determine nitrate nitrogen as described above, after first distilling off the ammonia. Cyanamide, dicyandiamide, and guanlylurea are also removed by this procedure.

Estimation of Perchlorate in Chile Saltpeter.—Occasionally potassium perchlorate occurs in Chile saltpeter. The method used for its estimation

¹ *Ind. Eng. Chem.*, **15**, 1175 (1923).

depends upon the results of the determination of the chlorine content of the material under investigation both before and after the decomposition of the perchlorate. The conversion of perchlorate of potassium is secured by simple ignition or by ignition after the addition of different reagents, as for example metallic lead, caustic lime, sodium carbonate or magnesium oxide. The following method is recommended by Seleckmann:¹

Place 5 grams of Chile saltpeter, in which the quantity of chlorine has been determined, in a porcelain crucible of about 40-50 cc. capacity, add 15-20 grams of lead borings, and submit to a gradually increasing heat. When the salt and lead are melted, stir the mass vigorously with a copper wire, so regulating the heat as not to cause a too rapid evaporation of the mass. When the mass begins to thicken and only a few bubbles of gas are escaping, increase the heat sufficiently to produce a dark red color on the bottom of the crucible and hold at this temperature for 1 or 2 minutes. After cooling, soften the melt, which now contains nitrate and chlorate, with hot water and wash into a beaker. Add 3-4 grams of carbonate of soda and gradually warm the mixture. After filtering add nitric acid to the filtrate to acidity and estimate the chlorine in the usual way with the nitrate of silver. From the amount of chlorine obtained, subtract that which was originally present. The difference is the chlorine due to perchlorate.

QUALITY OF ORGANIC NITROGEN

Two methods, the so-called neutral permanganate method and the alkaline permanganate method, have been devised for testing the quality of organic nitrogen in fertilizers. They do not measure the availability of the nitrogen, but merely aid in distinguishing between good and poor sources of organic nitrogen.

Methods for Testing the Quality of Insoluble Organic Nitrogen.—Methods for testing the quality of insoluble organic nitrogen developed from attempts to secure a method which would show the relative availability of various nitrogenous organic materials. S. H. T. Hayes tried permanganate of potash in 1895. John P. Street, in 1896, reported on a comparison of Hayes permanganate method with a pepsin-hydrochloric acid method. A comparison of the pepsin-hydrochloric acid method, acid permanganate method, and alkaline permanganate method, and the results of pot experiments were reported by Street in 1897. Davidson, Shiver, Perkins, Morse, and C. H. Jones studied various modifications of the permanganate methods, but the pepsin-hydrochloric was abandoned as too tedious and unsatisfactory. The alkaline permanganate method was adopted as provisional in 1904, and studies were discontinued until 1910,

¹ *Z. angew. chem.*, **11**, 101 (1898).

when C. H. Jones took up the work again, and C. L. Hare (1912), R. N. Brackett and H. D. Haskins continued it. The permanganate method developed into two distinct methods: the so-called neutral method and the alkaline method.

The neutral permanganate method includes the digestion of the insoluble organic nitrogen with a solution of permanganate of potash (containing sodium carbonate) under specified conditions, and subsequent estimation of nitrogen in the residue by means of the regular Kjeldahl method. The nitrogenous material which goes into solution is more available to plants than that which resists the action of the permanganate.

In the alkaline permanganate method the insoluble material is digested with alkaline permanganate, and the ammonia produced is distilled off. The material must be dissolved, and the nitrogen must also be converted into ammonia. A smaller quantity of nitrogen is converted into ammonia by the alkaline permanganate than is made water-soluble by the neutral permanganate. For details of the methods reference should be made to the latest edition of *Methods of Analysis*, A. O. A. C.

The alkaline and neutral methods were adopted in 1914. In 1916 H. D. Haskins¹ reviewed the method and reported vegetation tests and collaborative work. A brief review of the literature is given by Carlyle and Fraps² in 1927. An extensive study of the method was made by H. C. Moore and R. White³ in 1926, and by John B. Smith⁴ in 1927 and 1928.

Use of sodium carbonate in the neutral permanganate method.—The neutral permanganate method was first applied to unmixed materials, and as originally devised it did not call for the use of sodium carbonate. In 1912, Street⁵ found that the method did not give the same results as mixtures of nitrogenous materials with acid phosphate (superphosphate), as it did on the unmixed substances. He ascribed this to the acidity of the mixtures, and found that when sodium carbonate was added to the mixture, satisfactory results were secured. Since that time sodium carbonate has been used in the so-called neutral permanganate method.

Chemistry of the Decomposition.—Robinson and Winter⁶ discuss the decomposition process by alkaline permanganate. The action of alkaline permanganate solution upon proteids in fertilizers may be divided into

¹ *J. Assoc. Official Agr. Chem.*, **3**, 304 (1920).

² *Ibid.*, **10**, 188 (1927).

³ *Ibid.*, 202.

⁴ *Ibid.*, **11**, 191 (1928); **12**, 182 (1929).

⁵ *Ind. Eng. Chem.*, **4**, 437 (1912).

⁶ *J. Assoc. Official Agr. Chem.*, **5**, 446 (1922).

two steps. The first, the action of the alkali, *i. e.*, the hydroxyions, will result in a hydrolytic cleavage of the protein compounds and ultimately produce amino acids and acid amides. Another result of the alkali in the reagent employed is the decomposition of a portion of the acid amides present, with the liberation of ammonia. The acid amides furnish practically all the ammonia liberated directly by the action of the alkali, since only a small portion is given off by the other compounds as the result of the action of alkali alone. In short, the alkali of the permanganate reagent breaks down the complex organic nitrogenous compounds into simpler ones, namely amino acids and acid amides, and converts a portion of the latter into ammonia.

The second step in the process (which, of course, goes on simultaneously with the first) is the conversion of a fraction of the amino-acid nitrogen formed by the alkali into ammonia. The ultimate effect, then, of both alkali and permanganate is the production of ammonia, which is used as a measure of the value of the material under examination.

No doubt it is possible with the alkaline permanganate reagent to measure the total amounts of acid amide and amino-acid nitrogen obtainable from any substance if treatment is continued long enough. All of this nitrogen can be used by plants for food purposes, in some cases directly and in others indirectly after conversion into ammonia. Any nitrogen which can be so converted must be considered as being potentially available; its measurement presents no problem. The difficulty lies in the determination of that portion of this potentially available fraction which will be made available during a growing season.

A second point of fundamental importance in the use of the alkaline permanganate method is the fact that the concentration of the reagents, especially the alkali, is constantly increasing, until, at the end of the distillation, the speed of any reaction not already completed is presumably high. Thus any variation in time will produce corresponding variations in results. With the tendency on the part of the sample to foam badly, however, the digestion and distillation periods may be lengthened beyond the time prescribed. Robertson and Winter also studied the quantities of ammonia produced in various fractions of the distillate.

Some Important Details of the Methods.—Some important details of the methods, to which particular attention has been devoted, include the weight of the samples to be taken and the preliminary estimation of the water-soluble nitrogen.

When the methods were first studied a constant weight of substance was used (1 gram), but the results were not satisfactory. When a constant quantity of nitrogen was used, 45 or 50 mg., the results were found to be more satisfactory, and 50 mg. is now specified in the method. Occasionally those unfamiliar with the development of the method attempt to go back to the use of a fixed weight of sample.

The use of a fixed amount of insoluble organic nitrogen sometimes gives rise to difficulty in washing the sample. In some cases the preliminary preparation of the insoluble organic nitrogen requires the washing of several times the amount of substance used in the preliminary test, so that unless the washing is carefully carried out some of the soluble organic nitrogen may be left in the washed material, resulting in lower activity than the material really possesses. This condition is helped to some extent by the A. O. A. C. requirement of passing the material if it contains 0.3 per cent or less water-insoluble organic nitrogen. In case of doubt it is best to estimate the insoluble organic nitrogen on the same weight of material and under the same conditions specified in the permanganate test, and calculate the results from the quantity of nitrogen actually found. This procedure, however, really is in favor of low-grade material, since some of the nitrogen not washed out may be inorganic, or water-soluble organic material of good quality.

Study of Details of the Methods.—Several studies of the details of the methods have been made by White and Moore¹ and by John B. Smith.¹ Magruder observed that like results for water-insoluble nitrogen are not always obtained in collaborative work. The cause of such discrepancy, however, did not appear from Smith's investigation of the more obvious points of deviation from the directions. The results for water-insoluble nitrogen were in satisfactory agreement despite the following variations in technic: Wash water at 20° C. versus 25° C.; acid added to dry versus wet residue in the Kjeldahl flask; and the use of ten different brands of filter paper varying in texture, size, or time required for passage of 250 cc. of water through the sample. High results were secured by incomplete washing when less than 250 cc. of water was used. One brand of filter paper contained a significant quantity of nitrogen. The blank is made on the filter paper after washing several sheets with water.

The directions provided for weighing a sample calculated to contain 50 mg. of water-insoluble nitrogen on a 11 cm. filter paper and washing with 250 cc. of water at room temperature. This procedure was compared with

¹ *Loc. cit.*

one previously advocated by Jones in which it was specified that quantities of more than 4 grams be weighed into a small beaker and washed a few times by decantation before being transferred to the filter for completion of the washing. Nitrogen in this residue is not significantly lower than that obtained by the first procedure. The second procedure is more effective for washing a large quantity of material with a relatively small quantity of water.

Nitrogen was determined in the material transferred from the filter paper; the greatest deviation from the desired 50 mg. of nitrogen was a shortage of 2.1 mg., which for insoluble nitrogen having an activity of 75 per cent, would result in an error of 4.2 per cent. For extreme accuracy the quantity of nitrogen actually transferred to the Kjeldahl flask should be ascertained by washing duplicate portions of samples, transferring them to flasks as usual, and determining total nitrogen in one and active nitrogen in the other. The filter should not be transferred with the residue since the nitrogen left in the paper and in the unremoved residue was found to be well above 1 mg. Such nitrogen would not be included in the actual determination of active nitrogen.

Digestion and Distillation in the Alkaline Method.—It was found by Smith that approximately 60 per cent of the active nitrogen was distilled in the first 15 cc., 20 per cent rather equally distributed over the succeeding 60 cc., and 20 per cent in the final 20 cc. Five per cent of the nitrogen distilled was recovered in the last 5 cc. of distillate. The required volume of 95 cc. of distillate must be measured accurately and the distillation must be stopped promptly at this point.

The quantity of ammonia left in the condensers and recovered by subsequent washing of the tubes contains the equivalent of 0.4 per cent of active nitrogen in seventeen trials. The method does not provide for the inclusion of the nitrogen that remains in the condenser tubes.

Smith's preliminary work did not indicate significant differences caused by variations in time and temperature of the preliminary digestion or from the use or omission of 0.2 gram of paraffin, but there was a decided effect due to rate and time of distillation. In fifty carefully controlled distillations, an average of 18 cc. of distillate was collected in the first 15-minute period, 24 cc. in the second, 27 cc. in the third, and 26 cc. in the last.

The use of a piece of paraffin the size of a pea, weighing 0.2 gram, did not affect the results materially, neither did the use of a small drop, 0.02 gram, of mineral lubricating oil. There were, however, some low results which may possibly be ascribed to the reduction of a small quan-

tity of permanganate by the paraffin or oil, as discussed by Moore and White. Either oil or paraffin is of decided value in preventing frothing and makes possible a uniform rate of distillation. This advantage is considered sufficient to offset the small losses of nitrogen activity noted. Preference is given to the lubricating oil because it neither collects on the walls of the condenser nor clouds the filtrate as does paraffin.

Extension of the digestion period to 1 hour did not significantly affect the results, but a reduction of the temperature from 110° C. to 100° C. gave slightly lower activities. A 30-minute digestion period should be sufficient for mixed fertilizers, especially if lubricating oil is used to eliminate frothing.

Consistent differences, caused by variations in both the time and rate of distillation, were noted. Lengthening the period to 90 minutes increased the average nitrogen activity of the six samples by 5 per cent, while shortening the period 45 minutes decreased it by an equal amount. Either of these modifications was formerly allowable under the official directions.

Smith also found that results could be varied at will by changes in the rate of distillation at different periods within the stipulated 60 minutes. Thus, rapid distillation at the start, followed by slow distillation until completion of the 95 cc. required at the end of 1 hour, gave results that averaged 6 per cent below those found for the reverse of this process. The discrepancy is probably due to a longer exposure of the protein material, to a greater concentration of alkali and to a higher degree of heat in the first instance. Both these factors would increase the rate of protein hydrolysis and aid in a greater production of ammonia. Both the rate and time of distillation should be carefully controlled, and this is easily possible when some reagent, as oil or paraffin, is used to prevent frothing.

The escape of any undissolved ammonia from the condenser was prevented by conducting the distillate below the surface of the liquid in the receiving cylinder. When the distillate was allowed to drop from a delivery tube extending 1 inch within the mouth of the cylinder, an average loss for six distillations of 11.7 per cent of the ammonia was noted. Some adequate method of trapping undissolved fumes should be used.

The solution of alkaline permanganate of potash is likely to become weaker with age. In 1928 Smith¹ found that the weaker and older solutions are likely to give lower results than the stronger solutions.

¹ *J. Assoc. Official Agr. Chem.*, **12**, 172 (1929).

Permanganate Methods Merely Distinguish between Good and Poor Sources of Nitrogen.—Although the permanganate and pepsin-hydrochloric acid methods were originally devised for the purpose of estimating the availability of organic nitrogenous materials, and for many years the methods were discussed as methods for the determination of the availability of organic nitrogen, it has been recognized and emphasized that they really only distinguish between good and poor sources of organic nitrogen. C. H. Jones emphasized this fact when first presenting the alkaline permanganate method; he considered 50 per cent availability to be the dividing line. The alkaline method fails with cottonseed meal, uric acid, cotton pomace and Peruvian guano, which are recognized as good sources of nitrogen.

Interpretation of results by the permanganate methods.—The A. O. A. C. has adopted the following standards with respect to interpretation of results by the permanganate method:

The alkaline and neutral permanganate methods distinguish between the better and the poorer sources of water-insoluble nitrogen, and do not show the percentage availability of the material. The available nitrogen of any product can be measured only after carefully conducted vegetation experiments.

(a) The methods shall be used on mixed fertilizers containing water-insoluble nitrogen amounting to 0.3 per cent or more of the weight of the material. In the event of the total nitrogen exceeding the minimum guarantee, accompanied by a low activity of the insoluble nitrogen, the over-run may be taken into consideration in determining the classification of the water-insoluble nitrogen.

(b) The water-insoluble nitrogen in mixed fertilizers showing an activity below 50 per cent by the alkaline method, and also below 80 per cent by the neutral method, shall be classed as inferior. This necessitates the use of both methods before classifying as inferior.

This ruling recognizes the fact that either method alone may condemn good materials. For example, the alkaline permanganate method alone would condemn cottonseed meal. If the material does not pass both methods, very probably it is of poor quality. This ruling is, in fact, very liberal, perhaps a little too much so, but it is the best that can be done at the present time.

Vegetation experiments to test the availability of nitrogenous compounds should be made in a soil low in nitrogen, but which gives a good response when nitrogenous fertilizers are added. The soil should receive sufficient other fertilizing materials to assure that nitrogen is the limiting factor. Check pots receiving no nitrogen should be used, and also pots with a standard nitrogenous material. Nitrogen in two or more different

amounts of the various materials to be tested should be added. The same number of seeds should be planted. The crop should receive the same care, and be harvested and dried under the same conditions. Nitrogen should be estimated in the crops, since the percentage varies. The quantity of nitrogen in the crop grown without any fertilizer should be deducted from the quantities secured with the additions, and these should be compared with the standard material used. The results will depend somewhat on soil, season, and kind of crop.

Comparison with Vegetation Experiments.—A number of comparisons have been made between the permanganate methods for availability and the results of vegetation tests. Most of these, however, were made while the methods were in process of development. Hartwell and Pember¹ compared the availability of the water-insoluble nitrogen in 147 samples of fertilizer as measured by vegetation experiments with oats or millet, with the activity as secured by the alkaline permanganate method, and in some cases, by the neutral permanganate. In general, the methods did not condemn good materials.

H. D. Haskins studied a number of materials, using both the unwashed material and the substance which had been washed with water to remove water-insoluble material. The results are given for the purpose of showing the activity of some of the nitrogenous materials.

Each pot received 38 pounds of a mixture (one part loam soil deficient in nitrogen and three parts of sifted sand). The fertilizers were mixed with the entire amount of soil in each pot, the amount of each material used being as follows: 14 grams of fine ground limestone, 5 grams each of muriate of potash and potash-magnesium sulfate, 2.5 grams of high grade sulfate of potash, 18 grams each of 16 per cent superphosphate (acid phosphate) and basic slag phosphate. The nitrogen-containing materials were applied in unit quantity to supply 0.42 gram of nitrogen.

The experiment was run in two series to show (1) the availability of the total nitrogen and (2) the availability of the water-insoluble nitrogen. Necessary checks were run with double the amount of nitrogen from dried red blood, the standard nitrogen source, in order to prove that in the minimum nitrogen applications the full effect of the nitrogen would be secured. Checks were also run by using increased amounts of the basic fertilizer application (phosphoric acid and potash).

¹ *J. Assoc. Official Agr. Chem.*, 7, 55 (1923).

AVAILABILITY OF NITROGEN BY VEGETATION EXPERIMENTS AND ACTIVITY.

Source of Nitrogen	Unwashed		Washed	
	Average relative N availability— dried blood at 50 basis. (Vegetation experiment)	Comparative N activity —by chemical methods— Alkaline permanganate method	Average relative N availability— dried blood at 50 basis. (Vegetation experiment)	Comparative N activity —by chemical methods— Alkaline permanganate method
Dried blood, red	80	79	80	71
Dried blood, dark	79	84	92	84
Foreign nitrogenous tankage	62	64	53	48
Hoof meal	67	82	78	80
Peruvian guano	90	65	90	99
Milorganic	68	84	44	62
Imported process tankage	63	62	70	49
Process tankage	62	61	51	56
Whole guano	60	76	60	62
Dry ground fish	75	74	77	72
Cottonseed meal	66	62	57	97
Castor pomace	78	64	80	59
Packing house tankage	60	77	74	61
Packing house tankage	74	78	81	73
Uric acid	77	24	90	60
				24
				83

Water was supplied by both subirrigation and surface applications in amounts representing 50 per cent of the water-holding capacity of the soil mixture until hot weather, when it was increased to 60 per cent.

Japanese barnyard millet was the crop grown. All pots had 9 or 10 plants. The plants were analyzed, and the results compared on the basis of the nitrogen taken up in excess of that from the pots which received no fertilizer. Except for a number of process tankages sold under trade names the results are given in the table. It is interesting to note the low activity of uric acid by the alkaline permanganate method and its high activity by the neutral method.



Fig. 12.—Pot Experiments to Test Availability of Nitrogen Materials (Haskins).

FOREIGN OFFICIAL METHODS

GERMANY

Verband Landwirtschaftlicher Versuchs-Stationen im Deutschen Reich, Berlin, 1917¹

(1) **Ammonia Nitrogen.**—An aqueous solution should customarily be made and the ammonia distilled over from an aliquot portion with burnt magnesia, as free as possible from carbon dioxide, into titrated acid.

¹ Translated by Albert R. Merz. The numbers used in connection with the paragraphs are those given in the original copy.

(2) The result should be termed ammonia nitrogen. The terms, water-soluble ammonia nitrogen and total ammonia nitrogen, should be avoided. Any one, however, is permitted to add: "Determined in the aqueous solution."

(3) **Nitrate Nitrogen.**—The nitrate nitrogen should be determined by a direct method. In addition to the Kuhn method¹ the methods of Ulsch,² Devarda,³ Lunge,⁴ Schlosing-Grandeau,⁵ and Jodlbauer-Förster⁶ are recommended.

(4) **Organic Nitrogen.**—The nitrogen in organic form should ordinarily be determined by Kjeldahl's procedure. It is not suitable for pyridine and quinoline derivatives and should not be used in the presence of nitrates and nitrites except with certain modifications.

(5) The Kjeldahl procedure is customarily carried out in the modified form of Wilfarth with the addition of mercury. Instead of unmixed concentrated sulfuric acid, that to which phosphorus pentoxide has been added (up to 200 grams per liter) is also used, or the substance is first heated with concentrated sulfuric acid and mercury, according to the proposal of Gunning-Atterberg, and potassium sulfate (up to 18 grams for 20 cc. sulfuric acid) added after cessation of the foaming. It is necessary to subtract from the result the small quantities of ammonia in the reagents, ascertained by blank determinations with a nitrogen-free organic substance (1 gram of salicylic acid is preferred) that chars on heating with sulfuric acid. The caustic liquor must be free from nitrates and nitrites.

(6) **Nitrogen in Substances that Contain Ammonia-, Nitrate- and Organic Nitrogen.**—The ammonia nitrogen can be easily determined by distillation with magnesia, and its presence does not interfere with the determination of total nitrogen. The methods of Grandeau or Lunge or, after the ammonia has been distilled off, the reduction methods mentioned under (3), which may also be used for the determination of the sum of the ammonia and nitrate nitrogen, are especially adapted to the determination of nitrate nitrogen. The total nitrogen should be determined by the Kjeldahl-Jodlbauer-Förster procedure or by the Ulsch-Kjeldahl method.

The separation and determination of the various forms of nitrogen can present special difficulties, however, especially when easily decomposable nitrogenous organic substances are present. No general directions to overcome these can be given.⁷

*Special Directions for the Investigation of the Most Important
Fertilizer Materials*

AMMONIUM SULFATE

(30) **Ammonia Nitrogen in Ammonium Sulfate.**—Dissolve 10 grams ammonium sulfate in water to 1 liter. Distil 100 cc. (= 1 gram) of the solution,

¹ *Chem.-Ztg.*, 1899, pp. 196, 239, 255.

² *Ibid.*, 1890, p. 1410.

³ *Methodenbuch des Verbands der landwirtschaftl. Versuchs-Stationen in Österreich.* 1st ed., 1913, p. 45.

⁴ *Chem. Ind.*, 1881, p. 347.

⁵ Treadwell, *Lehrbuch der Analytischen Chemie*, II Band, 6th ed., p. 382.

⁶ *Chem. Ztg.*, 1889, p. 229.

⁷ On the determination of nitrate nitrogen compare Th. Pfeiffer and H. Thurmann, *Landw. Vers. Sta.*, 46, 1 (1895).

after the addition of about 200 cc. of water, with 3 grams of burnt magnesia. Note (1) and (2).

(32) **Sodium Nitrate and Calcium Nitrate.**—Dissolve 10 grams of the sample in water to 500 cc. Treat 25 cc. of the solution (= 0.5 gram of substance) according to (3).

(34) **Total Nitrogen in Calcium Cyanamide.**—It is difficult to prepare a correct average sample for analysis. Immediately after weighing, therefore, the sample prepared for analysis in the ordinary way should be ground again quickly and very carefully in a mortar. Too small quantities should not be weighed out (about 5 grams in best), and the material should be taken from a large number of places in the sample, which has been spread out. The total nitrogen should be determined by the Kjeldahl procedure. The sample in the flask should be slightly moistened with water before the addition of the concentrated sulfuric acid. Many materials apparently cannot endure the sudden strong heating caused by the addition of the concentrated acid. It is recommended, therefore, that more dilute acid be added first. It is also advisable to heat for some time with only a small flame.

(35) **Peruvian Guano.**—Attention is called to Peruvian guano frequently containing nitrate nitrogen, which should be considered in the determination of total nitrogen. One should proceed according to (6).

(41) **Ammonia-, Nitrate-, and Organic Nitrogen in Superphosphate Mixtures.**—For the determination of ammonia and nitrate nitrogen aliquot parts of the aqueous solution used for the determination of water-soluble phosphoric acid, in most cases 50 cc., corresponding to 1 gram of substance, are used. The determination of the organic and of the total nitrogen is made by the Kjeldahl method. To be taken into consideration in the nitrogen determination are (1) to (6) and the observation (35).

(54) **Nitrogen in Bone Meals, Guanos and other Materials Requiring Treatment with Acid for the Phosphoric Acid Determination.**—Proceed according to (41).

*Verein Deutscher Dünger-Fabrikanten
Braunschweig, 1925¹*

Standardization of the Acid and Alkali.—The strength of the sulfuric acid used for titration is advantageously chosen as half normal with 24.52 grams of H_2SO_4 per liter and that of the sodium hydroxide as fourth normal with 10 grams of NaOH per liter. Of the numerous substances proposed for standardization those considered the most reliable at present are sodium carbonate, sodium oxalate (Sørensen) and ammonium chloride. Congo red, methyl red and p-nitrophenol are mostly used today in addition to the older indicators, tincture of cochineal and methyl orange.

Indicator Solutions.—Two-tenths gram of Congo red is dissolved in 100 cc. of hot water, then filtered. To each 100 cc. of the solution to be titrated add 0.5 cc. of indicator solution.

Two-tenths gram of methyl red is dissolved in 100 cc. of alcohol. Add 2 drops of indicator solution to 100 cc.

¹ Translated by Albert R. Merz.

One-tenth gram of p-nitrophenol is dissolved in 100 cc. of water. Use 2 drops of indicator solution for 100 cc.

Standardization with Sodium Carbonate.—Chemically pure sodium bicarbonate is gently ignited in a platinum crucible, according to Lunge's¹ directions. The gases from the flame are diverted by placing the crucible in a circular opening of an asbestos plate, and contamination of the salt by the sulfur compounds of the illuminating gas is thereby avoided. The crucible may also be heated in a sand bath at 300°. Place about 0.5 gram of the ignited salt, weighed out exactly, with 200 cc. of water in an Erlenmeyer flask; place a small funnel on it, permit 25 cc. of the acid to flow in, and heat to boiling. After cooling titrate with the alkali. In addition, determine by titration how much alkali is required to neutralize 25 cc. of the acid. Na_2CO_3 (106.000) = N_2 (28.016). Therefore 1 gram of Na_2CO_3 = 0.26430 gram of N.

Standardization with Sodium Oxalate (Sörensen).—The anhydrous, non-hygroscopic salt $\text{Na}_2\text{C}_2\text{O}_4$ can be obtained from C. A. F. Kahlbaum of Adlerhof bei Berlin in an excellent state of purity. About 0.5 gram is weighed out accurately in a platinum crucible. Place the crucible in the perforated asbestos plate and first heat cautiously in the covered crucible in order to avoid spurting, then ignite about 20 minutes. In order to burn up any separated carbon, ignite a few minutes more intensely with the cover partly off. Place the cooled crucible with its contents, together with the cover, in a tall beaker to which 25 cc. of the acid has been added. Moisten the contents of the crucible with a little water, place a watch-glass upon the beaker, and bring the acid in contact with the salt by means of a rotary movement. Complete the decomposition by placing on a hot water bath and transfer the liquid to an Erlenmeyer flask, carefully washing the glass and the crucible subsequently. Remove the carbon dioxide completely by boiling, let cool, and titrate back.

$\text{Na}_2\text{C}_2\text{O}_4$ (134.000) = N_2 (28.016). Therefore 1 gram $\text{Na}_2\text{C}_2\text{O}_4$ = 0.20907 gram of N.

Standardization with Ammonium Chloride.—About 1 gram of the chemically pure and dry salt is weighed out exactly and distilled with a small excess of pure caustic soda, the receiver containing 40 cc. of the acid. The salt made by the Badische Anilin-und Soda Fabrik from synthetically produced ammonia is especially adapted to the standardization. $2\text{NH}_4\text{Cl}$ (107.000) = N_2 (28.016). Therefore 1 gram of NH_4Cl = 0.26183 gram of N.

Any of the above methods of standardization should be carried out at least 3 times and, in case of sufficient agreement, the average should be taken.

A. NITRATE NITROGEN

a. *Ulsch Method.*²—Twenty grams of the nitrate, or a quantity of mixed fertilizer containing about 20 grams of nitrate, are dissolved in 1 liter of water; 20 cc., corresponding to 0.4 gram of the sample, are placed in a distillation flask and 5 grams of iron (reduced by hydrogen) and 10 cc. of dilute sulfuric acid, sp. gr., 1.35 (obtained by mixing 2 volumes of water with 1 volume of concentrated sulfuric

¹ Taschenbuch für die Sodaindustrie. Technisch-Chemische Untersuchungsmethoden.

² Chem. Ztg., 1890, p. 1410.

acid) are added. The reaction starts at once. Careful warming is carried out later and finally more strongly to boiling. The reduction takes about 30 minutes. Losses by spurting liquid are to be avoided by setting a sealed spherical glass bulb on the flask. The walls of the glass vessel are now washed, about 150 cc. of water and 25 cc. of caustic soda, sp. gr. 1.30, are added, and the ammonia is distilled into the acid in the receiver. The quantities of nitrogen contained in the reagents are ascertained by blank determinations and considered. Reduced iron contains at times up to 0.3 per cent nitrogen. Furthermore it must be free from iron sulfide, as otherwise a violent evolution of hydrogen sulfide takes place and causes losses of nitrogen.

Small quantities of nitrite nitrogen are also determined, but loss of nitrogen takes place with larger quantities. This loss can be avoided, however, by the modification of Mach.¹ In this the solution under examination is previously allowed to run into boiling permanganate solution to oxidize the nitrite before beginning the reduction by the Ulsch procedure.

b. *Arnd Method.*²

REAGENTS

Copper-magnesium alloy.—It should contain about 60 per cent copper and 40 per cent magnesium. Slight deviations in the relative proportions of the two metals do not matter. The alloy is furnished by the Aluminium- und Magnesiumfabrik A.-G. at Hemelingen bei Bremen. It should be obtained in compact form and comminuted until it passes through a 1 mm. sieve. Owing to its inclination (even though slight) to oxidize, the powder should be kept in tightly closed containers and frequently prepared fresh from the dry, larger pieces that are also kept in this way. The alloy should be tested for freedom from nitrogen by blank determinations.

Magnesium chloride solution.—Dissolve 200 grams of crystallized magnesium chloride in water to 1 liter. To remove the small quantities of ammonia almost always present, boil the solution, after the addition of about 3 grams of burnt magnesia and several pieces of pumice, to about one-third its volume, strongly dilute with water, and evaporate again. Then bring again to the original volume and filter.

METHOD OF PROCEDURE

Dilute the neutral, or at most very slightly acid, solution of the nitrate, or nitrite, in a distillation flask to about 300 cc. and add 5 grams of powdered alloy and 10 cc. of magnesium chloride solution. Connect at once with the distillation apparatus, which has already been provided with the standard acid, and heat immediately with the full flame. The distillation must be continued until the ammonia has with certainty been driven off; an hour of boiling suffices in most cases.

The distillation apparatus must afford assured protection against the carrying over of droplets of the liquid into the receiver, even with a violent evolution of hydrogen. The small amounts of nitrogen due to the reagents should be determined by blank determinations and subtracted. Besides, it is advisable to carry out a further full control experiment with chemically pure ammonium chloride.

¹ *V. Angew. Chem.*, 1922, p. 473.

² *Ibid.*, 1917, p. 169 and 1920, p. 296.

Limits of Applicability.—The sum of the nitrate and nitrite nitrogen must not exceed 100 mg. Nitrogen already present as ammonium salt is also included in this determination without any loss, even if its quantity is somewhat larger than 100 mg. Admixtures of KCl, NaCl, CaCl₂, MgCl₂ and CaSO₄ up to 3 grams each are not harmful, but considerable quantities of easily soluble sulfates are. There must not be more than 300 mg. of SO₄ in the solution. Larger quantities up to 1.3 grams, however, do not prove harmful if the quantity of the magnesium chloride solution is increased to 50 cc. Small quantities of free acid do no harm, and larger quantities can be neutralized by the addition of burnt magnesia, an excess of which does no harm. Sodium or potassium hydroxides hamper the reducing power of the alloy when present even in small quantity. The preceding directions with 10 cc. of magnesium chloride solution are, therefore, to be used for all known nitrate- and ammonium nitrate-salts when using a solution containing 0.5 gram of the material. With nitrate-containing mixed fertilizers it is advantageous to use a quantity of solution corresponding to 1 gram of material. In exceptional cases (presence of much sulfate and much free acid) the addition of the larger quantity of 50 cc. magnesium chloride solution and of burnt magnesia may also be necessary. In both cases special care must be given to the distillation equipment; a spraying over of liquid and the formation of a dead space in the neck of the flask must positively be avoided.

Nitrite.—To determine the nitrite alone the aqueous solution of the material is allowed to flow, according to Lunge's procedure, from a buret into a measured permanganate solution of known strength, which has been acidified with sulfuric acid, diluted with water to 400 cc., and heated to 40°.

2 KMnO₄ = 5 nitrite nitrogen. In salts containing much nitrite nitrogen the nitrite nitrogen may be determined also by the methyl alcohol method of Fischer and Steinbach¹ or by the modification given by Mach and Sindlinger.²

c. *Indirect- nitrate determination in Chile saltpeter.*—Since the indirect or difference method is still standard for imports, it is given here. The importers determine insoluble, water, sodium chloride and sodium sulfate and calculate the remainder as nitrate; the importers at Hamburg are an exception as they also consider the perchlorate, report it as potassium perchlorate and figure it in up to 0.75 per cent. Any excess is deducted. The analytical procedure is as follows:

1. *Insoluble.*—Ten grams of the sample, ground and sieved as quickly as possible, are dissolved in 100 cc. of water, allowed to settle, filtered through a tared filter, and washed with warm water. The filter is dried and reweighed.

2. *Water.*—Ten grams of the sample, prepared as just stated, are dried in a porcelain crucible 2 hours at 130-140°.

3. *Sodium Chloride.*—Twenty grams of the sample are dissolved in a 250 cc. flask, filled to the mark and filtered; 50 cc. of the filtrate (= 4 grams saltpeter) are titrated as usual by the Volhard or Mohr method.

4. *Sulfates.*—Fifty cubic centimeters of the filtrate of Solution 3 (= 4 grams saltpeter) are slightly acidified with hydrochloric acid and precipitated hot with hot barium chloride solution. The BaSO₄ obtained is treated in the usual way and calculated to Na₂SO₄.

¹ Z. anal. Chem., 52, 393 (1913).

² Z. angew. Chem., 1922, p. 473.

5. *Potassium perchlorate*.—Twenty grams of the sample are soaked with about 6 cc. of a cold saturated soda solution in an iron or nickel dish of about 200 cc. capacity, about 1 gram of chlorine-free manganese dioxide is added and the contents of the dish are dried at a gentle heat; the contents of the dish are then brought to fusion over a strong Bunsen burner and the dish is heated for 15 minutes so strongly that it shows a dark, yet clearly visible, red heat; the dish is kept covered. After completed fusion, allow to cool, take up with hot water, bring the solution into a 250 cc. flask, fill to the mark after cooling, filter, and pipet off 50 cc. of the filtrate (= 4 grams saltpeter) into a beaker. Add 10 cc. of nitric acid (1.2 sp. gr.) and while rotating, drop in permanganate (40 grams per liter) to oxidize the nitrite that has been formed until the red color persists for a minute. After completed oxidation add 5 cc. of a cold saturated iron ammonium alum solution and titrate by the Volhard method. The difference between the number of cubic centimeters of 0.1 *N* silver solution used here and in determination 3, multiplied by 0.01386×25 , gives the percentage of KClO_4 .¹

For sales of saltpeter on the West Coast (of America) the Valparaiso analysis is standard. It determines sodium chloride (chloruro de sodio), sulfates (sulfatos), insoluble (materia insoluble), and moisture (humedad).

The difference to 100 is assumed to be nitrate (salitre). Perchlorate is not determined.

B. AMMONIA NITROGEN

1. **In Ammonium Salts.**—For the determination of ammonia in ammonium salts dissolve 20 grams of the well-mixed sample in a liter flask, shake frequently, and pipet 50 cc. (= 1 gram of material) from the solution, which need not be filtered, into a nitrogen flask of about 700 cc. capacity, add about 200 cc. of water and distil with a small excess of sodium hydroxide solution (about 5 cc. of 30 per cent). A 500 cc. Erlenmeyer flask, containing a sufficient quantity of standard sulfuric acid (40 cc. 0.5 *N*) is best adapted as a receiver. The flame is so regulated that the distillation is finished in about 45 minutes. Bumping can be lessened by the addition of a small knife point full of zinc filings. This should not be used in the presence of nitrogen compounds that give ammonia as a result of reduction. Small pieces of pumice stone, anthracite or other porous materials are then a suitable substitute.

2. **In Ammonium Superphosphates.**—a. *Older Conventional Method.*—Make use of the aqueous solution containing 20 grams in 1 liter which has been used for the determination of the water-soluble phosphoric acid and proceed as described under 1. Use the same indicator for titration of the acid in the receiver as has been used in the standardization of the acid and the alkali. Since in the case of certain ammonium superphosphates the shaking with water does not permit the finding of all the ammonia, either of the two following methods may be designated as standard.²

b. *Direct method*—Pour water over 5 grams of the ammonium superphosphate in a distillation flask and distil with a small excess of caustic soda. Use a 500 cc.

¹ In Rotterdam the saltpeter is also handled according to the difference method customary in Hamburg; in Antwerp and Dünkirkchen, however, on the basis of a 15.5 per cent nitrogen content.

² According to the decision of the 45th General Meeting of the Verband Landwirtschaftlicher Versuchs-Stationen im Deutschen Reiche.

volumetric flask containing standard acid as a receiver. After conclusion of the distillation bring to normal temperature, fill to the mark, mix, and titrate 100 cc. (= 1 gram material).

c. *Hydrochloric acid method*.—Allow 10 grams of ammonium superphosphate to stand in a Stohmann 500 cc. volumetric flask with 25 cc. of nitrogen-free 5 per cent hydrochloric acid for at least 3 hours, shaking occasionally. Fill to the mark and shake for a short time in a rotary shaking machine to mix uniformly. Use 50 cc., corresponding to 1 gram of material, for the ammonia distillation. Filtration is unnecessary. The hydrochloric acid requires an additional use of only about $\frac{1}{2}$ cc. of 30 per cent caustic soda.

C. NITROGEN IN ORGANIC MATERIALS

Combustion with soda lime was used formerly for the determination of nitrogen in the form of organic compounds. The Kjeldahl method is now generally used instead of this method. It has in the course of time undergone many modifications so that almost every laboratory uses its own modification. The Kjeldahl method depends on the conversion of nitrogen compounds into ammonia by heating with concentrated sulfuric acid in the presence of oxidizing materials. Place 1 gram of the material in a 600 cc. Jena nitrogen flask, add a drop of mercury (1 gram), and 15 cc. of concentrated sulfuric acid (1.84 sp. gr.). By adding phosphorus pentoxide (up to 200 grams per liter of sulfuric acid) the time of digestion is decidedly shortened. Heat at first with a small, and later with a larger flame, until the liquid has become colorless. After cooling add 250 cc. of water, cool, add quickly 80 cc. of caustic soda (1.30 sp. gr.) and, for precipitation of the mercury, 25 cc. of an aqueous solution of potassium sulfide (40 grams of Kalium sulfuratum per liter) and some zinc filings to prevent bumping. Join the flask and its contents as quickly as possible with the distillation apparatus and distil off the ammonia. About 30 minutes is required as a rule.

The Gunning-Atterberg modification of the Kjeldahl procedure is also recommended.—It follows: Heat 1 to 2 grams, until dissolved, with 20 cc. of nitrogen-free concentrated sulfuric acid with the addition of about 1 gram of mercury. This requires about 15 minutes. Then add about 20 grams of nitrogen-free potassium sulfate and boil again. After initial disappearance of the color continue the heating for 15 minutes more. In the case of substances that do not froth the potassium sulfate may be added immediately at the start. Distil the dissolved mass with caustic soda as described above. In some laboratories larger quantities of material and correspondingly larger quantities of reagents are used.

In many cases the Kjeldahl digestion may be hastened by the addition of hydrogen peroxide.¹

D. CALCIUM CYANAMIDE

In analyzing calcium cyanamide the preparation of an actual average sample for weighing is of primary importance. Every sample should be quickly ground and then spread out flat. For the weighing take portions from as many places as possible. The sample weighed should not be too small, about 5 grams is best.

¹ *Z. angew. Chem.*, 1921, p. 627 and *Landw. Vers.-Sta.*, 99, 150 (1922).

Determine the nitrogen by the Kjeldahl method. Moisten the sample in the flask slightly with water before adding the sulfuric acid.

Many materials do not seem to bear the sudden strong heating when the concentrated sulfuric acid is added. It is, recommended therefore, that some dilute acid be added first. It is also advisable to warm for a considerable time with only a small flame.

E. TOTAL NITROGEN

Organically combined nitrogen and any ammonia nitrogen present are determined by the Kjeldahl method. The presence of nitrate nitrogen requires one of the following modifications of the procedure.

a. *Jodlbauer method*.—Place 1 gram of the substance in a Kjeldahl flask with 25 cc. of phenolsulfuric acid (20 grams phenol in 1 liter of 1.84 sp. gr. sulfuric acid), shaking the flask slightly. Carefully cool the flask, cautiously and gradually add with constant cooling 2-3 grams of nitrogen-free powdered zinc and 1 gram of mercury, and digest by the Kjeldahl procedure until colorless. All the nitrogen compounds are converted into ammonia after 30-45 minutes of boiling. Cool, add water cautiously, cool again, and supersaturate with caustic soda to distil off the ammonia. The above described Gunning-Atterberg method of digestion with potassium sulfate can also be combined with this method.

b. *Förster method*.—Add 20 cc. of phenolsulfuric acid (200 grams of phosphoric anhydride and 40 grams of phenol per liter of sulfuric acid) to 1 gram of the mixed fertilizer in a digestion flask and dissolve with shaking. Then add 1-2 grams of dry sodium thiosulfate, 10 cc. of concentrated sulfuric acid, and 1 gram of mercury and boil until colorless. After the addition of water, caustic soda and potassium sulfide distil off the ammonia.

The total nitrogen in mixed fertilizers can also be ascertained by the Ulsch-Kjeldahl or Arnd-Kjeldahl procedures by first reducing the nitrite and nitrate and then digesting according to Kjeldahl.

FRANCE¹

(1) **Organic Nitrogen by Means of Soda Lime in a High-grade Fertilizer Containing no Nitrate**.—The organic nitrogen in fertilizers is converted to ammonia when the material is heated with soda lime. This reaction is the basis of the method of analysis here given. Nitrates do not permit of its use.

In a hard glass tube, well dried and closed at one end and 35-40 cm. long, place first, for a distance of 2 cm., calcium oxalate, then, for a distance of 5 cm., soda lime in small fragments, and introduce a mixture, made in a mortar, of 50 cg. of the material to be analyzed and coarsely powdered soda lime. (The mixture should not occupy more than 12-15 cm. in the tube.) Clean the mortar and the copper scoop used for introducing the material with small quantities of soda lime, then finish filling the tube up to 3 cm. of the extremity with soda lime in small pieces. Plug with sufficient asbestos to prevent any entrainment of the soda lime by the

¹ *Méthode d'Analyse des Engrais*. Ministère de l'Agriculture. Paris, 1897. Translated by Albert R. Merz.

disengagement of gases; wipe the interior edge of the tube carefully with paper and stopper with a cork; wrap around the tube a strip of metal foil, leaving the two extremities of the tube exposed for a distance of 4 cm.; fasten the foil with twisted copper wire; and replace the cork stopper with a rubber stopper containing a gas tube bent at a right angle and elongated. Place the tube in a gas or charcoal combustion furnace, then insert the elongated end of the delivery tube into a test tube containing 10 cc. of normal acid colored with a definite quantity of litmus. Plunge the elongated part to the bottom of the test tube. (A Will and Warrentrapp bulb tube may be used, but its use is not considered convenient.)

Commence to heat the open extremity of the tube; when this part is red proceed progressively toward the part containing the material, lighting the burners or bringing the charcoal closer so as to obtain a disengagement of bubbles that is regular and not too rapid. Continue this procedure until all the material has been decomposed, heating so that the tube reaches and keeps a dark red temperature but does not exceed it. Finally, when the evolution of gas has almost ceased, raise the temperature of the tube to a bright red and commence to heat gradually the part containing the calcium oxalate intended to furnish the hydrogen to remove the last traces of ammonia. When the evolution of gas has entirely ceased, by means of a wash bottle direct a jet of cold water on the anterior part of the tube while holding the delivery tube and test tube. After the hard glass tube breaks, remove the stopper and wash the delivery tube inside and out, receiving the wash water in the test tube. Next, transfer all the liquid to a flask and proceed to titrate by means of a potassium hydroxide solution, as would be the case in determining ammonia. Standardize the same against 10 cc. of normal acid and calculate as explained under the determination of ammonia.

When the fertilizer contains ammonium salts, part of the ammonia will be liberated when the mixture is made in the mortar. In this case, it is necessary to proceed very rapidly and to have the soda lime entirely pulverized previously. For the sake of safety the material can be triturated with some crystals of oxalic acid before it is mixed with the soda lime.

It would appear to be preferable to determine previously all the ammonia that would form by displacing it with magnesia and then working upon the residue for the determination of the organic nitrogen by means of soda lime; the determination, however, would be lengthened considerably. The precautions that have been indicated in order to avoid the loss of ammonia are sufficient.

Often the sample is not dry, and it is necessary previously to bring it to dryness, but if this desiccation is made without special precautions free or carbonated ammonia will be lost by volatilization; this would be the case with farm manure, liquid manure, etc. This inconvenience is avoided by adding to the material enough powdered oxalic acid to give a distinctly acid reaction to the mass; the ammonia is thus fixed as oxalate. Account is taken, in weighing the material used for the analysis, of the weight of oxalic acid.

PREPARATION OF THE SODA LIME

Place 600 grams of powdered slaked lime in a stoneware dish and pour over it a solution of 260 grams of caustic soda in 250 cc. of water. Make a paste, in-

introduce into a stoneware crucible, and heat to redness; remove the hot material from the crucible and crush it up rapidly in a copper mortar so as to have the pieces about the size of a pea and not excessively mixed with powder. Place this material while still hot in a well-stoppered bottle.

PREPARATION OF THE CALCIUM OXALATE

Place 100 grams of oxalic acid in a small copper pan and add sufficient boiling water to dissolve it; then add, in small portions, powdered slaked lime, stirring constantly until litmus paper shows that the lime has been added in excess; evaporate at first over an open flame, while stirring vigorously, and then complete the desiccation on a sand bath. Place the dried material in a well-stoppered flask.

(2) **Organic Nitrogen in Fertilizers Poor in Nitrogen and Containing No Nitrate.**—The determination by means of soda lime is carried out easily on fertilizers containing no nitrates. Take a gram of material and proceed as in the preceding chapter with the one exception—substitute for the normal titrated acid 0.1 *N* titrated acid and make use of lime water to neutralize the acid. (It may happen that the fertilizer is richer in nitrogen than was thought and, consequently, the 10 cc. of 0.1 *N* acid would be completely neutralized, which would cause a loss of ammonia. In this case, as soon as the litmus turns blue, it is necessary to add 10 cc. more of 0.1 *N* acid and finish the operation as before. Account is taken in the calculation of the 10 cc. of added acid.

(3) **Nitrogen in Materials That Are Lacking in Homogeneity and Are Difficult to Grind (Method of Grandean).**—It may happen that the nitrogenous fertilizer is in particles difficult to subdivide and different in nature; such is the case with cloth, leather, wool wastes, and so forth. It is then impossible to obtain a homogeneous mixture from which to take a quantity of material for analysis. In this case proceed as follows:

Treat 50 grams of the material to be analyzed in a porcelain dish with a quantity of concentrated sulfuric acid sufficient to impregnate the whole mass; heat on the sand bath, stirring frequently, until disintegration is complete. Then add, in small portions, finely powdered chalk until a solid mass has been obtained, grind in a mortar, and mix with care. (The acid is not completely neutralized with the chalk, so that no loss of ammonia takes place during the manipulation.) Take the weight of the powder thus obtained and weigh out one-tenth of it for the analysis; material corresponding to 1 gram of fertilizer is thus used. Treat this part with soda lime as if it were a question of an ordinary analysis; then, according to the supposed richness of the fertilizer, use normal or 0.1 *N* sulfuric acid. (This method is not applicable where nitrates are present.)

In cases where the determination is made by the Kjeldahl method, do not neutralize the acid, but take a definite fraction, as for example, one-fiftieth of the boiled acid obtained, corresponding to 1 gram of material.

(4) **Nitrogen in Its Three Forms in a Mixed Fertilizer.**—In practice, in the same fertilizer it is frequently necessary to determine nitrogen in the nitrate, ammonia, and organically combined forms. The determination of total nitrogen could only be made by means of a method that would measure the volume of the nitrogen. The ordinary procedure by means of soda lime would only give erroneous results.

It is often necessary to determine these different forms of nitrogen separately, especially when their commercial value is not the same; in order to fix the price of a fertilizer, it is necessary to know the proportion of each form:

A. Determination of nitric nitrogen.—Take 66 grams of the material and triturate in a mortar with a little water; extract with water, decanting the liquor into a liter volumetric flask and washing the residue many times, or until the volume has been brought to a liter and all the nitrate is in solution. Determine it as explained in the paragraph treating of the analysis of nitrates.

B. Determination of ammonia.—Introduce 1 gram into a Schloesing distillation apparatus; add 200 cc. of water and 1 gram of calcined magnesia; and distil, receiving in titrated sulfuric acid. If the fertilizer is rich in ammonia, use normal acid; if it is poor, use 0.1 *N* acid.

C. Determination of organic nitrogen.—Organic nitrogen is generally found in fertilizers in a soluble and an insoluble state. This nitrogen is determined under one form only but in making this determination soluble organic nitrogen would be lost if one proceeded to wash with water to eliminate the nitrates completely. It is proper to proceed as follows:

Place 2 grams of the fertilizer in a flat-bottomed dish, 9 cm. in diameter; add 10 cc. of ferrous chloride solution and 100 cc. of hydrochloric acid; cover the dish with a funnel in order to prevent spattering, bring quickly to a boil, and maintain until the nitrous vapors are completely eliminated. Then evaporate to dryness on a sand bath, stopping when the acid vapors cease to be evolved. (It is important not to prolong the heating action uselessly in order not to volatilize the ammonium salts.) Then add to the dish 4 grams of ground chalk, mix the mass so as to obtain a powder that can be easily removed, and carefully transfer it from the dish to a soda lime tube. Since the material is voluminous use a tube 40-45 cm. long and work very rapidly in order to avoid any loss of ammonia by volatilization. Carry out the operation as in an ordinary determination. In this treatment the ammonia has not been eliminated, and therefore the nitrogen found represents the sum of the organic nitrogen and the ammoniacal nitrogen. As the latter has been determined separately, subtract it from the figure found in this analysis and thus obtain the nitrogen that exists in the organic form.

(5) **Nitrogen by the Kjeldahl Method.**—This method is recommended for its rapidity and the ease with which a large number of determinations can be carried out. The principle involves the transformation of organic nitrogen into ammoniacal nitrogen by means of sulfuric acid with the addition of either dehydrated copper sulfate or red oxide of mercury, or more often, of metallic mercury, added initially. The liquid is then distilled with caustic soda solution free from any trace of carbonates and determination of the ammonia is made in the usual manner by means of standard sulfuric acid. This method is not applicable to cases where there are appreciable quantities of nitrates.

The treatment with the acid is carried out as follows:

In a 200-250 cc. flask, introduce 5 dg. or 1 gram of the sample and add about 1 gram of metallic mercury or 2 or 3 grams of dry, powdered copper sulfate. Pour upon the whole 20 cc. of pure mono-hydrated sulfuric acid. Heat it first gently, then more strongly and continue the boiling until the liquid has become entirely clear. (It is not necessary that the acid become completely free from color, but it

should be perfectly clear; 30-45 minutes of boiling generally is sufficient for complete transformation of the nitrogen into ammonia.) The liquid having become entirely clear, let it cool; cautiously add a little water, then a larger amount until 100 cc. has been added. Shake in order to dissolve completely the mercury salt that has settled on the bottom and transfer to a distillation flask, washing several times. The distillation flask has a content of nearly 1 liter. Add caustic soda solution in excess of the sulfuric acid. The final liquid is about 200-250 cc. It is desirable to add in addition 3 or 4 cc. of a saturated solution of sodium sulfide to precipitate the mercury and to prevent the formation of a difficultly decomposable compound of mercury and ammonia.

Owing to the evolution of hydrogen it is desirable to add a little granulated zinc to make the boiling more tranquil. Distil, and collect the ammonia that is evolved in standard sulfuric acid. To avoid the spattering and entrainment of the soda in the distilled liquid make use of a Schloesing apparatus, which can advantageously be given the form adopted by Aubin.

When the product to be analyzed contains nitrates, remove these by heating with ferrous chloride and hydrochloric acid and evaporating to dryness. This can be done in the flask in which the sulfuric acid digestion is made. A correction should be made for the traces of ammonia that may be contained in the sulfuric acid; it is made once for all for the same acid by a blank determination; it is ordinarily very small. It is necessary that the sulfuric acid be free from nitric compounds; a prolonged boiling completely eliminates the latter. It is also necessary that the caustic soda solution be free from nitrates, and the absence of these must be verified.

In the digestion 20 grams of powdered potassium sulfate may be substituted for the mercury or copper sulfate. The use of sodium sulfide is thus avoided, but the digestion is less rapid.

(6) Determination of Ammonia in Sulfate of Ammonia with the Schloesing Apparatus.—The determination of ammonia is always carried out by displacing this base with a fixed base and distilling, and the ammonia is collected in a standard acid; the extent to which this is neutralized measures the proportion of volatile alkali.

Weigh out 25 grams of the sulfate, dissolve in water, and bring the volume to 1 liter. Take 20 cc. of this solution, corresponding to 5 dg. of sulfate, by means of a calibrated pipet; introduce into the long-necked flask of the apparatus, and add 150 cc. of water and 2 grams of slaked lime or an equivalent solution of soda or potash. The flask is joined by means of a short rubber tube with a glass worm condenser. The condenser is provided with an elongated bulbed tube, the end of which dips 1-3 mm. or more into 10 cc. of normal sulfuric acid, contained in a small flask. The apparatus being thus arranged and the water circulating in the condenser, heat the flask to boiling. The ammonia escapes at once and combines with the normal sulfuric acid; it may happen that in consequence of a too rapid absorption of the ammonia the acid liquid will rise in the tube, but this will cause no inconvenience because the bulb is sufficiently large to contain it. Continue to heat so as to distil off slowly a quantity of water sufficient to remove the last traces of ammonia; when the quantity of distilled water has reached 60-80 cc., detach the bulb tube from the apparatus and then extinguish the flame; wash the interior of

the bulb tube and its exterior end with small quantities of water, collecting in the flask. Then titrate with an alkaline solution.

Preparation of the standard sulfuric acid.—Place pure distilled sulfuric acid in a platinum dish; bring to a boil and maintain this heat for 30 minutes; and then let the dish cool under a ground bell jar in order to avoid the absorption of any trace of moisture. (The dish should be placed on an iron tripod to avoid breaking the glass plate on which the bell jar stands.) The acid having been cooled, pour about 50 cc. of it rapidly into a glass-stoppered flask which has been weighed on a precision balance; stopper immediately; take its weight; and pour the acid into a graduated flask, washing to remove all the acid that has been weighed. Dilute the volume so that 61.25 grams of the sulfuric acid is contained in exactly 1 liter. This solution is called normal acid. The liquid thus obtained is carefully mixed and preserved in a glass-stoppered flask. Since the glass often has an alkaline reaction and since part of the acid will be neutralized by this alkalinity of the glass, flasks in which concentrated sulfuric acid has stood a long time should be chosen. This method for the preparation of the standard acid is not the only one that can be used, but it appears to be convenient.

Preparation of 0.1 N acid.—Pour 100. of the normal sulfuric acid into a liter volumetric flask and bring the volume to 1 liter with distilled water that has been previously boiled.

Preparation of the potassium hydroxide solution.—Dissolve 100 grams of potassium hydroxide in 3.6 liters of water and add 50 grams of slaked lime. After solution and several hours' contact, filter into a well-stoppered bottle.

Preparation of the lime water.—Place 200-300 grams of slaked lime in a 5 liter, stoppered bottle; fill with water; shake; and, after settling, pour off the water that has dissolved the salts which the lime might contain. Add water again, shaking from time to time. Filter this lime water into a bottle for use, avoiding access of air as much as possible. Close with a stopper provided with two tubes drawn out at the end and bent at right angles; the one serves for pouring out the lime water and the other for the entrance of air. These two tubes are themselves stoppered with small rubber tubes provided with glass valves.

Preparation of the magnesia.—Triturate in a mortar commercial block magnesium carbonate; make a homogeneous paste of it by adding successive small quantities of water; introduce this liquid paste into a bottle of distilled water; and decant the supernatant liquid from time to time, replacing it anew with distilled water and shaking frequently. (This operation removes the alkalies that are generally admixed and might act upon the nitrogenous organic matter.) Transfer to a funnel plugged with a wad of cotton; let drain; dry in the oven; place in a stoneware crucible; and calcine for an hour at a faint red heat. The product thus obtained is preserved in well-stoppered bottles. It is well to calcine the quantity necessary for the determination just prior to its use in order to expel traces of ammonia that the magnesia may have absorbed.

Test for sulfocyanides in sulfate of ammonia.—It sometimes happens that sulfate of ammonia, especially that coming from the manufacture of illuminating gas, contains ammonium sulfocyanide, a substance that is exceedingly poisonous to plants as well as to animals. Since use of this product may have a disastrous effect upon crops, substances containing it must be rejected. It is sufficient to make a qualita-

tive test for the presence of this compound. All sulfate of ammonia in which its presence is confirmed should be considered unsuitable for agricultural use. Make the determination as follows: Dissolve a small quantity of the sulfate of ammonia in water; add several drops of a dilute solution of ferric chloride which immediately gives a beautiful characteristic red color.

(7) **Ammonia in Mixed Fertilizers.**—Mixed fertilizers generally contain, besides ammonium salts, nitrogenous organic matter; if lime were used to expel the volatile alkali, as for sulfate of ammonia, there would be danger of converting part of the organic nitrogen into ammonia and the determination would therefore be inaccurate. To prevent this action, replace the lime by magnesia, which has only an extremely feeble action upon nitrogenous organic matter. The procedure is the same as for sulfate of ammonia; 1 gram of the fertilizer is used with about 1 gram of calcined magnesia. If the fertilizer is rich in ammonium salts, use normal sulfuric acid and titrate with potassium hydroxide. If, on the contrary, the fertilizer is low grade, replace the normal sulfuric acid by 0.1 *N* sulfuric acid and titrate with lime water.

The method of distilling the material directly with water and magnesia sometimes encounters difficulties, especially when large quantities of material containing very little ammonia are used. Such is the case with farm yard manure, for example. In applying the flame directly under the flask there is danger of superheating the material that collects on the bottom and thus producing ammonia from the nitrogenous organic matter. This can be avoided completely by using a calcium chloride bath into which the flask is dipped. The bath is heated so as to cause boiling of the liquid in the flask.

It is preferable in many cases to extract the ammonia by washing and to distil the liquid thus obtained after it has been made alkaline with magnesia, instead of distilling the material itself.

When there is little organic matter in the substance to be analyzed, the extraction can be made with water, but otherwise, particularly in the case of the brown material of manures, a part of the ammonia will be retained in insoluble combinations; it is then necessary to use water slightly acidulated with hydrochloric acid to destroy the combination of this material with ammonia and bring the ammonia into solution. In the latter case it is necessary to saturate the acid with an excess of magnesia before proceeding to distil.

The precaution of treating previously with an acid is indispensable when magnesium ammonium phosphate exists in the material. This compound is only difficultly decomposed by magnesia when it exists in a solid state, but when it has been previously dissolved in an acid it gives up its ammonia easily under the influence of magnesia.

When acid is used, a considerable quantity of material, for example 50 grams, may be employed; in this case decant the liquid into a 1 liter calibrated flask, washing the residue several times until a volume of 1 liter is reached. Mix this liquid, take a definite fraction, either 20 cc., corresponding to 1 gram of material, or more if the quantity of ammonia is small.

The standard acid in which the ammonia is to be determined ought never to be in contact with the air for a long period of time because this might increase the

proportion of this alkali. Much more, the proximity of ammoniacal vapors ought to be avoided during the manipulations.

It sometimes happens that during the operations the water that distils entrains carbonic acid, which remains dissolved in the distilled liquid. The titration is then uncertain, and it is necessary, before titrating, to remove this carbonic acid. This is done by heating to boiling for some minutes the liquid in the flask and by taking care to avoid all spattering. The determination is then carried on as before.

(8) **Nitric Acid in Nitrates.**—The procedure, called *by difference*, which is still used in commercial transactions, should be proscribed because it does not offer sufficient guarantees of exactness. The only method that ought to be employed is based upon the transformation of all the nitric acid into nitrogen dioxide, which is collected in the gaseous state and measured by volume; it is applicable not only to commercial nitrates, but also to fertilizers to which nitrates have been added.

The volume of dioxide that is formed is compared with that given by the same quantity of perfectly pure nitrate; the ratio of the two volumes gives the actual proportion of nitrate contained in the product under examination. But in order that this comparison may lead to exact results it is necessary to make all the conditions of operation, and, consequently, the relative errors, as nearly equal as possible. This is done by contriving to obtain closely similar volumes of nitrogen dioxide in two cases. With this end in view, first make the test with the material to be analyzed; the volume of nitrogen dioxide having been read, employ a quantity of standardized, pure nitrate liquor so as to give a nearly equal volume.

Preparation of the Ferrous Chloride Solution.—Dissolve, while boiling, 200 grams of tacks or iron filings in a flask with hydrochloric acid, dilute with an equal volume of water, added gradually until completely dissolved, and bring the volume of the liquid to 1 liter

Analysis of sodium nitrate—Prepare a standard solution, containing 66 grams of pure, dry sodium nitrate per liter; also take 66 grams of the nitrate to be analyzed, dissolve, and bring to a volume of 1 liter. This quantity has appeared convenient because it allows for a volume of gas approximately 100 cc. The apparatus in which the operation is carried out is a 150 cc. flask provided with a two-hole rubber stopper carrying a capillary tube 20 cm. long, which extends several centimeters from the bottom of the flask so that the bottom of the tube is always above the liquid. The other end of the tube is connected by heavy rubber tubing to a small funnel.

There should be a distance of 25 cm. between the end of the tube and the stem of the funnel; a clamp is placed on the rubber tubing. The other opening of the stopper carries a gas tube, bent at right angles and connected by rubber tubing to another bent tube. The part of this second tube that dips into the water ought to be 20-30 cm. long in order to condense the water vapor; it dips into a small trough filled with water. If a series of determinations is to be made, it is well to let water flow constantly into this trough so as to displace, to some extent, the water that has become hot and charged with hydrochloric acid and to maintain a constant level. Into the flask first pour 40 cc. of ferrous chloride solution; stopper and, by means of the funnel, add 40 cc. of hydrochloric acid, pinching the rubber tube at the moment when a little hydrochloric acid still remains in the funnel. This operation is for the purpose of avoiding imprisonment of air in the capillary tube

or the stem of the funnel. (This air would be entrained in the apparatus and would affect the volume of the nitrogen dioxide.) The apparatus being thus arranged, place a ring gas burner under the flask and heat to cause regular boiling; the air is expelled and bubbles through the tube. When all the air has been expelled by boiling 5-6 minutes and only water vapor, which condenses on contact with the cold water, is evolved, place over the bent end of the tube a 100 cc. graduated bell glass completely filled with water; then pour into the funnel by means of a calibrated pipet 5 cc. of the nitrate solution to be tested and, slightly opening the clamp, let this liquid flow slowly into the flask so as not to stop the boiling. Close the clamp before the liquid has reached the stem of the funnel, then wash with several cubic centimeters of hydrochloric acid which is poured, by means of an elongated tube, upon the whole upper periphery of the funnel. This liquid is introduced, in its turn, with the same precautions; renew the washing three times, taking constant care to avoid entrance of any air. (The constant boiling in the flask liberates nitrogen dioxide, which collects under the bell glass.) Prolong the boiling until the volume of gas no longer increases; then, without stopping the boiling, withdraw the bell glass and by sinking it more or less bring the level of the water in it to the level of the water in the trough. (Care must be taken to hold the bell glass with tongs and not with the hand.) After waiting some minutes to let the gas assume the temperature of the surroundings, read the volume (V) occupied by the gas in the bell glass. Fill the bell glass anew with water and place it over the end of the tube, maintaining the vacuum in the flask by continued boiling. Introduce by means of the funnel 5 cc. of the standard solution of pure nitrate and proceed in exactly the same manner, taking the same precautions as in the preceding operation. Collect the nitrogen dioxide again and read its volume as has just been indicated. Let V' be the second volume obtained, then the ratio $\frac{V'}{V} \times 100$ will give the actual quantity of nitrate contained in 100 parts of the material tested.

Five or six consecutive determinations can be made without renewing the liquid in the flask and without discontinuing the boiling; under these conditions the determinations are made very rapidly, but it is necessary to take precautions to maintain the liquid in the flask constantly at a volume approximately equal to the original volume, liquids that are introduced replacing those which disappear as a result of the boiling. If the concentration becomes very strong it is necessary to add enough hydrochloric acid to bring it back to the desired volume.

Analysis of potassium nitrate.—For the analysis of a nitrate of potash proceed exactly in the same manner, but prepare the solutions by dissolving 80 grams of pure nitrate as well as of the nitrate to be tested in a volume of 1 liter. This figure is calculated likewise to give a volume of gas approximating 100 cc.

Sodium nitrate in a mixed fertilizer.—1. *Fertilizer rich in nitrate.*—Take 66 grams of fertilizer, grind in a glass mortar, and treat in the same manner with water; pour the liquid into a liter flask and wash the fertilizer several times. Bring all the decanted liquids together in the calibrated flask; bring the volume to 1 liter; and work with this clear solution (filtered if necessary), containing the nitrate, as if with a nitrate of soda, but instead of introducing only 5 cc. of the liquid into the flask take several times 5 cc., according to the grade of the fertilizer, so as not to have a volume of nitrogen dioxide much smaller than 100 cc. Let n be the

number of pipets of 5 cc. used; let V^1 be the volume of the gas obtained with 5 cc. of the standard solution of pure sodium nitrate and V the volume of the gas obtained with the material, then the quantity of nitrate contained in 100 parts of the fertilizer will be $\frac{V}{nV^1} \times 100$.

2. *Fertilizer poor in nitrate.*—Take 66 grams of the fertilizer, grind in a mortar, mix with water, allow to stand for several minutes, and decant the supernatant liquid into a 1 liter calibrated flask; wash the residue remaining in the mortar several times; and continue transferring the supernatant liquid to the calibrated flask until the volume has reached 1 liter.

Mix this liquid and add slaked lime in small portions until the liquid turns red litmus paper blue. Take 500 cc., evaporate in a porcelain dish, and bring the volume exactly to 50 cc. Then proceed with this liquid as for the fertilizer rich in nitrate. The calculation is made in the same manner, but it is necessary to divide the result obtained by 10. The addition of lime prevents the nitric acid being displaced by free sulfuric or phosphoric acids when a superphosphate is present.

When a fertilizer is exceedingly poor in nitrate, that is to say when it contains scarcely 1 per cent, the analyst can stop at a smaller volume instead of continuing to add the solution to the flask until approximately 100 cc. of nitrogen dioxide has been obtained. The calculation is made in the same way. To calculate to nitric nitrogen multiply the sodium nitrate by 0.1647.

Remark.—It sometimes happens that the fertilizer contains soluble carbonates. In this case the carbonic acid, which is evolved at the same time as the nitrogen dioxide, increases the volume of this gas and consequently leads to too high results. The presence of these soluble carbonates can be ascertained by mixing 10 grams of fertilizer with 20 or 30 cc. of water, transferring to a filter, and pouring a little hydrochloric acid into several cubic centimeters of the filtered liquid; if bubbles of gas are evolved, the presence of soluble carbonates is indicated. In this case, instead of triturating in the mortar with pure water, use water containing 3 or 4 per cent of hydrochloric acid. When all effervescence has ceased and the liquid remains acid, continue the washing with more water until the volume reaches 1 liter and continue the procedure as indicated above; but when it is necessary to subject the liquid to evaporation, it is not possible to work with an acid liquid for nitric acid would be lost, in which case, having brought the neutral or alkaline liquid to a very small volume, decompose the carbonates by the addition of acetic acid; only after this has been added bring the volume to 50 cc. and continue the determination as above. The carbon dioxide, having been eliminated, can no longer cause erroneous results.

Some fertilizer materials, such as guanos, may contain oxalic acid. Partial decomposition of this acid may produce carbonic acid and carbon monoxide which would go with the nitrogen dioxide and thus render the determination inaccurate. It is easy to obviate this cause of error by adding to the material, before solution, a little lime, which keeps the oxalic acid insoluble as calcium oxalate. The clear liquids in which the nitrates are determined are thus completely free from oxalic acid.

CHAPTER VI

POTASH

By B. B. ROSS,* LL.D., *Professor of Chemistry, Alabama Polytechnic Institute, Auburn, Ala., and State Chemist of Alabama*, and COLIN W. WHITTAKER, Ph.D., *Associate Chemist, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.*

The element potassium occurs in most rocks, in practically all natural waters, in saline deposits, in plants and in animal organisms. Because it is so widely distributed, it follows that potassium occurs in many fabricated products and in the waste material of many industries. It has been estimated that the average potassium oxide content of the earth's crust is 3.2 per cent and that the surface of the earth to a depth of one meter contains 3.9×10^{13} metric tons.¹ Potassium is seventh in the list of elements that make up the ten-mile crust of the earth, and eighth in a list of those that make up the hydrosphere, while the average potassium content of known terrestrial matter, including the atmosphere, is 2.40 per cent. The percentage for sodium, 2.63, is only slightly higher.²

Potassium salts removed from the mines at Stassfurt in the course of rock salt production were originally discarded as worthless; it was not until about 1858, when Francke and Liebig demonstrated the importance of potassium to agriculture and to various other industries that any importance was attached to the potash content of these deposits.

Use of the Term "Potash."—The term "potash," which is a contraction of the words pot and ash, originally referred to the ash or residue left in the pot when the lixivium of wood ashes was evaporated. This crude potash was chiefly potassium carbonate, and the term potash is still sometimes used when potassium carbonate is meant.

The German term Kali is analogous to potash, and has a similar history. The plants burned by the Arabians for the production of crude alkali were known as herba kali, kali being the Arabian word for ashes.

Because potassium compounds are used principally in the production of fertilizer and the elements in combination with the potassium are generally of no importance for this purpose, the practice of selling such fer-

* It is with the greatest regret that we announce the death of Dr. B. B. Ross on April 4th, 1930, after a long illness.—*Editor*.

¹ M. Camille Matignon, *Revue Sci.*, 57, 225-30 (1919).

² F. W. Clarke, *Data of Geochemistry*, 5th ed., 1924, p. 36.

tilizer salts on the basis of their equivalent in potassium oxide (K_2O) was begun. In this way the word potash has now come to mean K_2O , and in analyzing for potassium it is customary to report in terms of K_2O rather than in terms of potassium itself. When reference is made to the K_2O content, however, the expressions "potash content" or "actual potash" are generally used.

Prices on crude potassium salts, *e. g.*, kainite, muriate, etc., are quoted as so much per "unit." Since the unit is 20 pounds of potassium oxide, or one per cent of a ton, it is very simple to figure the cost per ton. Thus, if a crude potassium salt that analyzes 30 per cent potash (K_2O) is quoted at 60 cents a unit the price per ton of crude salt is 18 dollars.

Since all potassium compounds may be regarded as sources of potash, that is K_2O , the term potash has frequently been applied, perhaps loosely, to any of the crude commercial salts of potassium, and the industry concerned in their production and sale is known as the potash industry. In this chapter the term has been used freely in this broader sense as well as in the more restricted sense as meaning specifically K_2O .

A third meaning occurs frequently in trade literature where potash is often synonymous with potassium, *e. g.*, muriate of potash for potassium chloride, caustic potash for potassium hydroxide, and so on.

WORLD SUPPLIES OF POTASH

The chief commercial sources of potash may be classified as follows: (1) Soluble potash minerals; (2) insoluble potash minerals; (3) vegetable or organic sources; and (4) industrial wastes of both inorganic and organic nature.

The first group includes *subterranean deposits*, such as those of Stassfurt, and *surface deposits* like the potassium nitrate deposits of India. Potash brines, such as the brine of Searles Lake, are included. Feldspar and leucite are examples of the second group. The third group includes such sources as Caucasian sunflower, wood ashes, etc. Cement dust, wool scourings and distillery waste are examples of the fourth group.

Obviously the groups overlap at times, as in the case of blast furnace potash where the source is an insoluble potash-bearing mineral used in the manufacture of pig iron, but where the potash is recovered from otherwise waste material.

SOLUBLE POTASH MINERALS

Soluble potash minerals, which have long been the principal source of potash, occur in subterranean deposits and in those on or near the surface. They are usually mined with ease, and their potash content is sometimes high enough to permit marketing of the crude mineral without processing; if processing is required it involves little expense compared to the insoluble potash minerals. In surface deposits the potash is sometimes contained principally in a brine that fills the interstices of a bed of other salts. Natural brine lakes, such as Great Salt Lake, where all the salts present are in solution, are included in this group.

SUBTERRANEAN DEPOSITS

Important subterranean deposits occur in Germany, France, Spain, Russia, Poland, the United States, and other countries. Each of these will be considered according to its importance and the available information.

Germany (Stassfurt).--The salt or brine springs near Stassfurt furnished the natives of the surrounding country with salt in the thirteenth century and earlier. Agricola in his "*De ortu et causis subterraneorum*" (Basil, 1546) expressed the opinion that these springs must have their origin in subterranean salt deposits, but no attempt to reach the salt was made until three centuries later. Karsten¹ in 1838, thought that rich saline beds would be reached by drilling in the neighborhood of the springs. A boring was started in 1839 in a search for rock salt. The saline bed was reached in 1843, at about 768 feet, but to the great disappointment of the drillers the salt was found to be a mixture of magnesium and potassium compounds. The presence of rock salt was demonstrated by later borings and a shaft was sunk in 1851 to mine this salt. The overburden of potash and magnesium salts, called *abraumsalze* (*abraum*, refuse; *salze*, salts), was rejected as worthless, but this waste did not continue long because about this time the importance of potash as a plant food was emphasized by Liebig and interest in potash as a fertilizer was aroused to such an extent that these salts became of prime importance. A. Francke erected the first plant for the extraction of potassium chloride in 1861; three more factories entered the field in 1862, and the four plants refined 20,000 tons of crude salts in that year. The industry developed rapidly.

¹ *Lehrbuch der Salinenkunde*, Berlin, 1846-7.

These deposits have been systematically explored. They extend to the "States of Thuringia on the south, with Hanover on the west, and Mecklenburg on the north, and underlie an area of more than 100 square miles. It has been estimated that the Stassfurt deposits occupy a volume of 10,790,000,000 cubic meters, containing 20,000,000,000 metric tons of potash salts, a quantity, at the present rate of consumption, sufficient to supply the world for 2,000 years."¹

Origin of the Stassfurt salts.—The Stassfurt beds are considered to be of marine origin, with contributions from fresh water streams that emptied into an ancient sea that is supposed² to have extended from the Ural Mountains to the Scandinavian Mountains and Ireland. The climate was torrid and evaporation rapid. This sea dried up in Germany, and it was here that its burden of salts was deposited. The order in which salts are deposited when sea water is evaporated corresponds roughly to the geological succession observed at Stassfurt. The deposition of these salts has been exhaustively studied and forms the basis of many important papers.³

The Stassfurt strata.—The order of deposits at Stassfurt is roughly as follows, going from the surface down:⁴

1. *Drift*, about 8 meters thick.
2. *Shales, sandstones and unconsolidated clays*, varying thickness.
3. *Younger rock salt*, thickness very variable, sometimes missing.
4. *Anhydrite*, rarely lacking, 30-80 meters thick.
5. *Salt clay*, average thickness 5-10 meters, very rarely absent.
6. The *carnallite* zone from 15-40 meters thick. At Douglasshall a layer of rock salt intervenes between the carnallite and the clay. In parts of the field kainite overlies the carnallite, is itself overlain by sylvinite or hartsalz and that in turn by schoenite. These subzones are often missing.
7. The *kieserite* zone.
8. The *polyhalite* zone.
9. *Older rocks salt and anhydrite*. Nos. 7, 8 and 9 have a total thickness ranging from 150 to perhaps 1000 meters. The anhydrite forms layers, averaging 7 mm. thick, separating the salt into sheets of 8 or 9 cm.

¹ H. M. Hoar, Potash, Trade Promotion Series No. 33, Bur. Foreign and Domestic Commerce.

² Walther, *Centr. Mineral Geol.*, 311, (1902).

³ See papers by Van't Hoff and his coworkers, also see the monograph by E. Jenecke, *Die Entstehung der deutschen Kalisalzlager*, 2nd ed., Braunschweig, Vieweg & Sohn, 1925.

⁴ F. W. Clarke, *loc. cit.*, p. 223.

These layers have been interpreted as annual deposits, due possibly to seasonal variations in temperature or to alternating drought and rain. If this supposition is correct a Stassfurt salt bed 900 meters thick would require 10,000 years to form.

10. *Anhydrite and gypsum.*

Composition of the deposits.—More than 30 saline minerals are found in the Stassfurt deposits. Some of these are primary minerals, and others are derived from the primary minerals by secondary reactions; a few are simple salts, but the majority are double compounds. A partial list follows.

IMPORTANT MINERALS OF THE STASSFURT DEPOSITS.

Halite (or rock salt)	NaCl
Sylvine (or sylvite)	KCl
Douglasite	$2\text{KCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$
Bischofite	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Tachhydrite	$2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$
Carnallite	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$
Thenardite	Na_2SO_4
Glauberite	$\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Leonite (or potassium astrakanite)	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Astrakanite (or bloedite)	$\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Schonite (or picromerite)	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Epsomite (or reichardtite)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Kainite	$\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$
Polyhalite	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Langbeinite	$2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$
Krugite	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Vanthoffite	$\text{MgSO}_4 \cdot 3\text{Na}_2\text{SO}_4$
Löwite	$\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$
Anhydrite (or karstenite)	CaSO_4
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Glaserite (or aphthitalite)	$3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ (variable)
Boracite (or stassfurtite)	$2\text{Mg}_3\text{B}_6\text{O}_{18} \cdot \text{MgCl}_2$
Sulphoborite	$\text{Mg}_4\text{H}_4\text{O}_{12}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$, or $2\text{MgSO}_4 \cdot 4\text{MgHBO}_4 \cdot 7\text{H}_2\text{O}$
Pinnoite	$\text{MgB}_3\text{O}_6 \cdot 3\text{H}_2\text{O}$
Ascharite	MgHBO_4 or $3\text{Mg}_2\text{B}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$
Heintzite	$\text{Mg}_4\text{K}_2\text{B}_{10}\text{O}_{22} \cdot 14\text{H}_2\text{O}$
Hydroboracite	$\text{MgCaB}_4\text{O}_{11} \cdot 6\text{H}_2\text{O}$

The theoretical composition of the important potash minerals is given in Table I.

The fertilizer materials (Kalidüngemittel) produced or mined at Stassfurt, may be divided into raw salts (Rohsalze), of which there are generally four, and processed salts, which include manure salts of various grades, muriate of potash, and sulfate of potash. This classification, with analyses of the materials, is shown in Table II.

TABLE I. — THEORETICAL COMPOSITION OF POTASH MINERALS.

	KCl	MgCl ₂	K ₂ SO ₄	MgSO ₄	Na ₂ SO ₄	CaSO ₄	H ₂ O	K ₂ O
Carnallite	26.83	34.27					38.91	16.9
Glaserite			71.04		28.96			38.4
(Variable)								
Kainite	29.94			48.35			21.71	18.9
Krugite			19.91	13.75		62.22	4.12	10.8
Langbeinite			41.90	58.01				22.7
Leonite			17.52	32.83			10.65	25.7
Polyhalite			28.90	10.97		45.16	5.97	15.6
Schonite			43.27	29.89			26.84	23.4
Sylvite	100.0							63.2
Syngenite			53.06			41.45	5.49	28.7

Kainite, sylvinite and carnallite are the names of specific minerals, but in the trade they take on a somewhat different meaning.¹ Each is used to designate a raw salt, of which the most important constituent is the mineral whose name it bears. Thus kainite refers to a naturally occurring mixture of the mineral kainite ($\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$) with rock salt (NaCl); sylvinite refers to a mixture of sylvite (KCl) and rock salt; carnallite refers to a naturally occurring mixture of carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), and rock salt (NaCl) with unimportant amounts of clay, anhydrite, boracite and other minerals.

The term hartsalz is applied usually to a mixture containing sylvite, kieserite and rock salt as important constituents. Hartsalz that contains langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$), kainite and carnallite also occurs.

Processing of the Raw Salts.—From a quarter to one-half of the weight of the raw salts carnallite, kainite, hartsalz and sylvinite consists of sodium chloride, which is not valuable as a fertilizer and is in many cases harmful, since some plants are sensitive to chlorine. In some cases, therefore, it becomes necessary to treat the raw salts to eliminate sodium chloride and other impurities, *e. g.*, magnesium sulfate, as well as to reduce shipping costs. This processing of the raw salts also gives opportunity for the production of by-products that would otherwise be lost. Since the method of processing differs somewhat with the location and the market utilized the following description will serve merely as a general outline.

Any of the raw salts, carnallite, hartsalz or sylvinite may be subjected to a simple process of solution and crystallization, which will yield, according to the conditions, a muriate of 65-95 per cent potassium chloride. Although the contaminating sodium chloride may be so completely removed by washing with water as to give a pure muriate containing at least 98 per cent potassium chloride, as a rule the working conditions are so chosen that the product has the desired composition after simple drying

¹ See also definitions adopted by the A. O. A. C., *J. Assoc. Official Agr. Chem.*, **12**, 61 (1929).

TABLE II. — POTASH FERTILIZER MATERIALS *

	KCl Per cent	MgCl ₂ Per cent	K ₂ SO ₄ Per cent	MgSO ₄ Per cent	CaSO ₄ Per cent	H ₂ O Per cent	Insoluble matter		K ₂ O Per cent
							NaCl		
<i>Raw salts</i>									
Kainite	20.5	—	—	36.4	1.7	16.5	24.1	0.8	13.0
Hartsalz	20.5	2.3	—	20.8	1.8	5.7	46.3	2.6	13.0
Sylvinite	27.6	1.8	—	3.4	2.8	4.5	56.7	3.2	17.4
Carnallite	15.5	21.5	—	12.1	1.9	26.1	22.4	0.5	0.8
<i>Potash fertilizer salts</i>									
Manure salts, at least 20 per cent K ₂ O	33.3	4.2	—	12.0	2.1	4.2	40.2	4.0	20.9
Manure salts, at least 30 per cent K ₂ O	48.6	4.2	—	10.2	2.2	5.1	26.2	3.5	30.7
Manure salts, at least 40 per cent K ₂ O	64.1	1.1	—	5.5	2.4	2.6	21.2	3.1	40.4
<i>Muriate of potash</i>									
Muriate, 90-95 per cent KCl	91.7	0.2	—	0.2	—	0.6	7.1	0.2	57.8
Muriate, 80-85 per cent KCl	83.5	0.3	—	0.4	—	1.1	14.5	0.2	52.6
<i>Sulfate</i>									
Potassium sulfate, at least 96 per cent K ₂ SO ₄	0.3	0.4	97.2	0.7	0.3	0.7	0.2	0.2	52.7
Potassium sulfate, at least 90 per cent K ₂ SO ₄	1.6	1.0	90.6	2.7	0.4	2.2	1.2	0.3	49.9
Potassium magnesium sulfate, at least 48 per cent K ₂ SO ₄	—	—	50.4	28.0	3.4	7.1	3.5	7.6	27.2

* Information supplied by the Kali Syndicat, Berlin.

of the crystallized salts. The other salts in the raw potash salts are only slightly dissolved and are seldom present in the finished product in concentrations sufficiently high to be troublesome. The mother liquor from the solution of the sylvinite and hartsalz is saturated with potassium chloride, sodium chloride, magnesium chloride and magnesium sulfate and can be reused for the treatment of a fresh batch of raw salts.

The treatment of crude carnallite is more complicated. The crude ore is heated with the mother liquor from a preceding extraction. This liquor contains magnesium chloride chiefly, and at its boiling point it readily dissolves the potassium chloride of the carnallite while most of the sodium chloride and magnesium sulfate associated with the crude carnallite remains undissolved. The hot liquid is allowed to cool slowly and potassium chloride of 64-69 per cent purity crystallizes out. The impurities are chiefly sodium chloride (about 20 per cent), magnesium chloride and bromide. This crude muriate can be washed with water to yield a purer product if desired. The mother liquor from the potassium chloride is evaporated and cooled. It yields pure artificial carnallite, which is treated like the crude carnallite, but it gives almost pure potassium chloride on the first crystallization. The mother liquor from the artificial carnallite precipitation may be returned to the process, but it is often used for the preparation of magnesium chloride, bromine and other substances.

Potassium sulfate is manufactured from kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and potassium chloride. The kieserite is dissolved in water, and potassium chloride is added, which causes the precipitation of potassium magnesium sulfate ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) as a crystalline precipitate. If this salt is then further treated with potassium chloride and water, potassium sulfate is precipitated. A purity of 90-98 per cent is readily obtained.

Manure salts are essentially a mixture of sodium and potassium chlorides. They contain from 20 to 40 per cent K_2O .

France (Alsace).—Potassium salts were found at Dornachs, 21 miles northwest of Mulhouse, as early as 1869, but the deposits now being worked were discovered by Vogt and Grisez in 1904 while drilling for coal in the forest of Nonnenbrück. Following this discovery a company was formed to explore the region by drilling. The borings made (approximately 165) showed the presence of a large deposit of potassium salts, chiefly sylvite, underlying an area of about 68 sq. miles. These deposits, described by Hoar as the most important thus far located in Alsace, lie in the south of the province in the plain bounded on the south by the Jura, on the west by the Vosges and on the east by the Rhine. They con-

sist of two strata, the more important occurring at a depth of 650-1000 meters. The average thickness is 4 meters and the bed extends over an area of 200 sq. km. The upper stratum lies 15-20 meters above the second and has a potassium chloride content of about 35 per cent; the second stratum is of lower potash content, but it is much more extensive. It is estimated that these beds contain over 300,000,000 metric tons of pure potash. The average potash content of the German crude salts is about 12 per cent, while those of Alsace average about 22 per cent, a figure that greatly favors the latter deposits. The analyses of crude and manufactured Alsatian potash salts, reported by Hoar, are given in Table III.

TABLE III.—ANALYSES OF ALSATIAN CRUDE AND MANUFACTURED POTASH SALTS.

	K ₂ O	KCl	NaCl	K ₂ SO ₄	MgSO ₄	CaSO ₄	H ₂ O	Insol- uble matter
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Kainite (sylvinite)	15	22-24	62-65	—	0.15	2.5	1.15	10.2
Manure salts	20-22	32-34	53-55	—	0.16	2.1	1.34	9.4
do	30-32	49-50	38-39	—	0.10	1.5	1.00	7.2
Muriate of potash	50	81.3	9.7	—	0.80	—	1.80	6.4
do	52	85.8	7.6	—	0.70	—	1.90	4.0
do	56.2	91.1	4.5	—	0.60	—	1.80	2.0
do	59.6-60	97.3	2.0	—	0.20	—	0.30	0.2
Sulfate of potash	50.6	—	1.35	93.65	0.80	0.9	2.10	1.2

Spain.—Spain possesses large subterranean deposits of potash-bearing salts at Cardona and at Suria in the Province of Barcelona. The reserves at Suria are estimated at 20,000,000 tons of pure K₂O.¹ At Cardona the deposits must be worked in the axis of a steep anticline, and the continuity of the beds is often broken by faulting. Similar difficulties exist at Suria.² These obstacles, however, have not prevented the development of these salts as shown by the production for 1927, which was 35,000 tons K₂O.

Russia.—Salt wells have been exploited in the region about Solikamsk since the reign of Ivan the Terrible, in the sixteenth century. In 1922, Prof. A. Chernov advanced the hypothesis that deposits of rock salt at a considerable depth caused the brine in the wells. Prospecting for potash by boring was started, but little progress was made until 1925. An immense deposit was discovered about Solikamsk on the left bank of the Upper Kama, at the base of the eastern slope of the Urals, north of Perm, and it was roughly delimited by borings. Faulting is uncommon, and

¹ H. S. Gale, *Eng. Min. J.*, **108**, 758-63 (1919).

² A. Holmes, *Geol. Mag.*, **6**, 254 (1919).

there seems to be good reason to believe that the region is underlain with a vast bed of salts containing 1500-1700 million tons of K_2O . At Solikamsk workable deposits start at a depth of 95 meters and extend to 200 meters. The beds consist of the following deposits: (1) rock salt at a depth of 80-90 meters; (2) sylvine, 8-20 meters thickness; (3) carnallite, 60-70 meters through; (4) sylvine, 30 meters thick; and (5) impure rock salt, the extent of which is still unknown.

These reserves appear to be nearly as large as any in the world, but no production has been reported to date. Considerable activity is reported in the Solikamsk¹ region and production will probably occur shortly.

Poland.—The Kalusz deposits of Galicia (Poland)² appear to underlie an area 76 km. long and 3-4 km. wide. Incomplete exploration indicates a total K_2O content of 10-12 million tons.³ The potash occurs principally as kainite, sylvite and carnallite. Production was small under Austrian control, but it is mounting rapidly under the new regime (2,344 tons of crude salts in 1913, compared to 275,456 tons in 1927).

United States.—In America attention is being given to the possibility of finding deposits of potash similar in nature to those in Alsace and Stassfurt, which have long supplied the world. Knowledge of a tremendous salt deposit resulting from the evaporation of an old sea in the south-central part of the United States gave stimulus to this search. This deposit underlies approximately 70,000 square miles in Texas and New Mexico and is reported to contain 50,000 billion tons of salt in those two states alone.⁴

The U. S. Bureau of Mines and the Geological Survey are exploring this region and attempting to locate workable potash beds. Fortunately, the region contains many oil wells, and much information has been obtained from oil well borings, although they are not often suitable for such exploration. The churn drills so mix the materials from adjacent strata or from strata separated by several feet that an analysis can indicate little more than the presence or absence of potash.

Owing to this difficulty funds were appropriated for drilling several wells with core drills, a type that yields a true cross section of the strata with a minimum of mutilation or mixing. This work is now under way, but only a small part of the area has been prospected in this manner. The deposits that have been found are not of great thickness nor are they

¹ D. M. Mushketov, *Econ. Rev. Soviet Union*, **11**, No. 23, 2-4 (1927).

² W. Kolski, *Z. landw. Versuchsw.*, **17**, 892 (1914).

³ J. W. Turrentine, *Mineral Ind.*, **38**, 528 (1929).

⁴ H. M. Hoots, U. S. Geol. Survey Bull., **780 B**.

rich in potash, but they are definitely of commercial value and of sufficient importance to lend further impetus to the search. In the light of present knowledge no useful estimates of the K_2O reserves in this region can be made.

Netherlands.—Potash deposits occur at Winterswijk and near Wessel in the Province of Overijssel. No estimate of these reserves is available at present.

India.—India possesses deposits of potash associated with the halite of the Salt Range. The potash seams are fairly numerous and run from $\frac{1}{2}$ to 2 meters thick, with a K_2O content of 6.8-14.4 per cent. Reserves are probably not large.

Canada.—Potash has been reported in the Malagash rock salt deposit in Nova Scotia and in Gautreau, New Brunswick. Both deposits are believed to be too small for commercial purposes.

SURFACE DEPOSITS

Surface deposits of soluble potash minerals are extremely varied in character. They range from brines of low potash content to beds of nearly pure potassium nitrate. These are considered in two groups, foreign and domestic deposits.

FOREIGN DEPOSITS

Surface or near surface saline residues occur in many foreign lands. Many of these would be important as reserves if war or other conditions should cut off supplies from the principal potash producing countries. Domestic production also is receiving encouragement in many lands, and these deposits take on importance for that reason. These foreign and domestic sources will be described in some detail.

Abyssinia.—The Piano del Sale of Abyssinia is the exposed, basin-like surface of a large saline deposit. Its salt beds are due to evaporation of an arm of the Red Sea that was permanently or intermittently cut off by the volcanic hills of the coast from the main body of water. Sylvite occurs at the surface over an area of 200,000 sq. yds. and varies from 2 to 5 feet in depth. The average potassium chloride content of this part of the deposit is 80 per cent. Surrounding the sylvite and extending over ten times the area and to a depth of 150 feet, is a deposit of carnallite with an average potassium chloride content of 15-25 per cent. The production of potassium chloride from these deposits is reported by Holmes to have been 50,000 tons in 1918.

Hoar has recently described this deposit, which lies mostly in a depression 200 feet below sea level, as follows: "At the surface is found potassium chloride of 90 per cent purity, the quantity of this salt being estimated at 140,000 metric tons. The lower layers carry from 40 to 80 per cent of the chloride and have been estimated at 1,860,000 tons of 95 per cent potassium chloride." The mining of this deposit is exceptionally easy, but transportation costs are very high.

Tripoli.—Two saline lakes in Tripoli near Bu Kammasch are reported to contain potassium salts in workable quantities. The larger of these, Lake Briga, lies partly in Tunis. It has been estimated to contain 250,000 metric tons of magnesium salts. The other, Lake Numa, is much smaller than Lake Briga.¹

Tunis.—A salt lake, south of Gabes, in Tunis is a source of both bromine and potash. A product known as sebkainite, reported by Holmes as containing about 34 per cent potash is obtained by solar evaporation of the brine. Production in 1919 was reported to be 1000 tons of potassium chloride monthly. The lake has an area of about 15,000 hectares.

Chile.—The dry saline lakes, Pintados and Bella Vista, in the province of Tarapacá, Chile, contain deposits of potassium chloride in some cases as rich as 36 per cent. The reserve is estimated at 2,000,000 tons and is 3-12 per cent chloride.² The potassium nitrate of caliche is mentioned elsewhere.

Brazil.—Saltpeter deposits have been reported from several localities in the valley of the São Francisco River. These deposits occur in limestone caverns or with other salts in beds of former lakes.

Deposits of potassium nitrate, 24 miles from Morro do Chapeo, in the Province of Bahia are said to be of great extent; the crude salt is 75 per cent potassium nitrate and is easily brought to 99 per cent purity by crystallization, according to Hoar.

South Africa.—Small scattering surface deposits of saltpeter (potassium nitrate) occur in the mountains in various parts of South Africa. These deposits have been ascribed to the habit of the "dassies" or rock rabbits of depositing their dung in particular localities. The dung is rich in nitrogen and it is conceivable that when the deposit is made on rocks containing a base, lime or potash, nitrates will form. One nitrate deposit in the Transvaal supplied the old Boer Government with saltpeter for making gunpowder.

¹ E. Niccoli, *Giorn. chim. ind. applicata*, **7**, 187-194 (1925).

² Kestner, *J. Soc. Chem. Ind.*, **37**, 291 (1918). See also S. Salcedo, *Chem. Trade J.*, **57**, 179 (1915).

Potassium nitrate also occurs in shale beds in South Africa that cover an area of some hundreds of square miles. The nitrate layers are not less than 10 feet thick, and the nitrate constitutes at least 3 per cent of the shales.¹ Little definite information about these deposits has come to hand.

India.—The Behar section of the Gangetic plain of India is famous for its production of saltpeter. The population of this region, which is over 500 to the square mile, is mainly agricultural in occupation and thus is accompanied by a high proportion of domestic animals, so that the soil is amply supplied with organic nitrogen. Wood and cow dung are used for fuel with the result that the soil around the villages is also well supplied with potash. These conditions, combined with a suitable climate, result in the formation of potassium nitrate in the soil. Saltpeter and other salts often effloresce at the surface during periods of dry weather.

Crude potassium nitrate is produced by simple methods. The salts are dissolved out of the soil and separated roughly by crystallization into the two principal constituents, sodium chloride and potassium nitrate. The saltpeter is then sent to refineries for further purification. Behar for many years yielded 20,000 tons of saltpeter annually,² but the records of the U. S. Bureau of Mines show a production for 1924 of only 8,680 tons of nitrate.

Mexico.—Small deposits of potassium nitrate have been reported from several localities, but they are believed to be small.

Guatemala.—Crude saltpeter is prepared from surface soil in villages in Guatemala in the districts of San Augustin, Progreso, Occidente, and Totonicapan.

Peru.—A deposit containing 5,000,000 tons of 49 per cent potassium chloride has been reported from Santa Ana in the Province of Arequipa. The salts occur in a vein about 18 inches thick under about a foot of conglomerate, in what appears to be an old lake. Scattered potassium nitrate deposits are reported from several localities.

Dead Sea.—In recent years interest in the exploitation of the Dead Sea for substances contained in its brine has been keen. Its potassium chloride content has been estimated at 1,300,000,000 tons,³ which in addition to vast quantities of sodium chloride and other substances is accompanied by 853,000,000 tons of magnesium bromide. The salinity of the Dead Sea is given by Enrico Niccoli as 22.30 per cent, 4.57 per cent of which rep-

¹ E. G. Bryant, *J. Soc. Chem. Ind.*, **38**, 360-2 T (1919).

² *Records Geol. Sur. India*, **46**, 210-15 (1915).

³ J. W. Turrentine, *Mineral Ind.*, **36**, 490 (1927).

resents the potassium chloride content. This is a very dilute brine compared with that of Searles Lake, where the total salinity is about 33 per cent and the potassium chloride content is nearly 12 per cent of that.

DOMESTIC DEPOSITS

The chief domestic surface deposits of potash salts are brines that occur in beds of other salts. One such brine, that of Searles Lake, is the basis of the largest potash industry in the United States.

Searles Lake.¹—Searles Lake basin is situated in San Bernardino County, Calif.; it lies between the Argus Range on the west and north-west, and a narrow rocky wall, known as the Slate Range, bounds it on the east and separates it from the deeper depression of the Panamint Valley. The basin is broad and roughly circular, 20-25 miles from north to south and 8-10 miles from east to west. At one time it was flooded to a depth of over 600 feet above the level of the present bottom. The present "lake" is an expanse of dry salt during the greater part of the year with an area of approximately 12 square miles and an average thickness of 65-75 feet. The salt surface is so hard and compact that teams and motor trucks cross it readily, but like that of other saline lakes, the salt body is extremely porous, and the pore space, except for a few inches at the surface, is filled with brine. The brine can be pumped almost indefinitely from one spot without affecting its level. It is estimated that this deposit² contains 20,000,000 tons of potash and 25,000,000 tons of sodium tetraborate.

Mineralogy of Searles Lake.—The following is an incomplete list of minerals occurring in the salt body. Their solubility is indicated.

Halite	NaCl	Very soluble
Mirabilite	Na ₂ SO ₄ .10H ₂ O	Very soluble
Thenardite	Na ₂ SO ₄	Very soluble
Trona (Urao)	Na ₂ CO ₃ .NaHCO ₃ .2H ₂ O	Readily soluble
Natron	Na ₂ CO ₃ .10H ₂ O	Very soluble
Borax	Na ₂ B ₄ O ₇ .10H ₂ O	Very soluble
Gypsum	CaSO ₄ .2H ₂ O	Slightly soluble
Anhydrite	CaSO ₄	Slightly soluble
Glauberite	CaSO ₄ .Na ₂ SO ₄	Slightly soluble
Hanksite	9Na ₂ SO ₄ .2Na ₂ CO ₃ .KCl	Readily soluble
Northupite	MgCO ₃ .Na ₂ CO ₃ .NaCl	Slightly soluble
Pirssonite	CaCO ₃ .Na ₂ CO ₃ .2H ₂ O	Slightly soluble
Gaylussite	CaCO ₃ .Na ₂ CO ₃ .5H ₂ O	Slightly soluble
Sulphohalite	2Na ₂ SO ₄ .NaCl.NaF	Slightly soluble
Tychite	2MgCO ₃ .2Na ₂ CO ₃ .Na ₂ SO ₄	Almost insoluble
Searlesite	Na ₂ O.B ₂ O ₃ .4SiO ₂ .2H ₂ O	Almost insoluble

¹ For material in this section the writers are particularly indebted to Hoyt S. Gale, U. S. Geol. Survey, Bull. 580, 251-323 (1913).

² J. W. Turrentine, Potash, p. 77 John Wiley & Sons, 1926.

Celestite, cerargyrite, colemanite, dolomite, embolite, gold, niter and sulfur have also been reported. A deep well drilled at Searles Lake has been a prolific source of unusual and entirely new minerals.¹

Chemical composition of Searles Lake brine.—Practically all the potassium is in the brine, which is of remarkable uniformity in composition from top to bottom and in all parts of the deposit. Two analyses are given in Table IV. The first is the average of six determinations made by W. Van Winkle of the Geological Survey, and the second is a more complete analysis made by W. H. Ross of the Bureau of Chemistry and Soils, U. S. Department of Agriculture.

TABLE IV.—CHEMICAL COMPOSITION OF SEARLES LAKE BRINE

	1	2
Total anhydrous salts, ignited residue, per cent	33.30	32.85*
Specific gravity of brine	1.2974	
Composition of salt, anhydrous residue, per cent		
Na	33.19	33.57
K	6.22	6.06
Li		0.01
Mg	0.00	Trace
Al ₂ O ₃		0.012
Fe ₂ O ₃		0.003
SiO ₂	0.02	0.023
Cl	36.39	37.02
Br		0.094
I		0.004
SO ₄	12.76	12.96
CO ₃	7.11	6.70
PO ₄		0.30
As ₂ O ₃	0.06	0.083
B ₄ O ₇	2.45	3.00
	98.20	99.830

* Approximate. Specific gravity of sample was not determined.

These analyses are made somewhat more intelligible by assigning the elements and radicals to each other in the conventional manner as follows:²

	Per cent
KCl	11.56
Na ₂ SO ₄	19.17
Na ₂ B ₄ O ₇	3.89
Na ₂ CO ₃	11.84
NaCl	51.96
Na ₂ HPO ₄	0.45
	98.87

¹ For a detailed description of these minerals see Gale's paper, p. 296-308

² Based on Ross' analysis, calculated by the writers.

The American Trona Corporation (now The American Potash and Chemical Corporation) started the erection of an experimental plant at Searles Lake in 1914. After extensive study and research, large scale production was reached in 1916. During the war other plants were con-

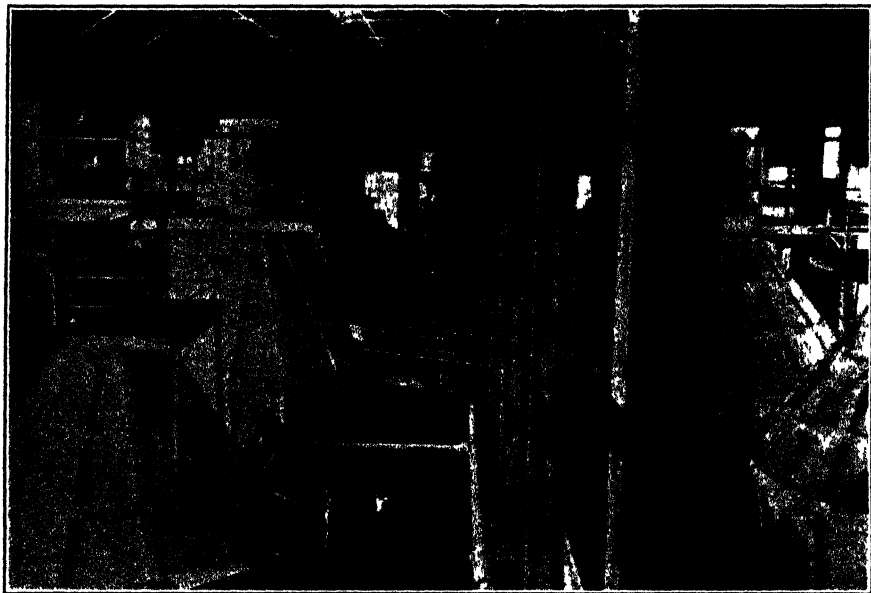


Fig 1 --Evaporating Room of the Searles Lake Plant of the American Potash and Chemical Corporation, showing Triple Effect Evaporators.

structed and operated, but they have since been dismantled. The American Potash and Chemical Corporation, on the other hand, has rebuilt and enlarged its plant and today is America's largest potash producer. Although the brine is extremely complex, it has been possible by means of a simple, rapid, economical process to obtain remarkably pure products and to continue to operate successfully in spite of the present low price of potash.

The process¹ employed at Searles Lake consists essentially in eliminating sodium chloride, sodium sulfate and sodium carbonate by evaporating the brine to the point where the liquor is nearly saturated with potassium chloride and sodium tetraborate. The liquor is cooled rapidly by boiling

¹ G. R. Robertson, *Ind. Eng. Chem.*, **21**, 520-524 (1929).

in vacuum, which results in the crystallization of a large part of the potassium chloride, which is removed in settling tanks, centrifuged till free from mother liquor, and then washed. After drying the potassium chloride is ready for shipment. The mother liquor from the potassium chloride crystals is carbonated and cooled first by water and finally by refrigeration, which brings about the crystallization of most of the borax. The borax is then subjected to a second crystallization for purposes of purification and after drying is ready for shipment. The various mother liquors still contain some potash and borax and are returned to the process. The sodium chloride, sulfate and carbonate are washed back into the lake.

Production in 1928 was 88,000 tons of potash, 20 per cent of the total consumption of the United States,¹ and 47,000 tons of borax. This plant is said to be the world's largest single producer of borax.

Great Salt Lake Desert.—The greater part of western Utah and small parts of adjacent States were once covered by Lake Bonneville,² of which Great Salt Lake is probably a remnant. As the waters of Lake Bonneville subsided a number of closed basins took the place of the single basin, and Great Salt Lake Desert is the central depression of one of these basins. It is situated between latitude 40° and $41^{\circ} 31'$ and between longitude 113° and the Nevada-Utah boundary at an approximate longitude of $114^{\circ} 2.5'$. The greater part lies in Tooele and Boxelder Counties, Utah. The desert is quite flat, but it contains several small groups of hills. This region has recently been prospected for potash by the Geological Survey,³ and the Survey's report supplies most of the information given here.

Two areas of crystalline salt occur in this desert. The larger of these, known as Salduro Marsh, covers nearly 150 square miles and is located near the west central border of the desert. The smaller deposit lies in the northwest corner of the embayment between the Desert Range and Pilot Mountain and is about 25 square miles in extent. The thickness of the salt bed of Salduro Marsh is about 5 feet near the central portion of the deposit, but it tapers off at the edges. The salt is extremely porous, and the pore space, except for a few inches at the surface, is filled with brine. The salt itself contains relatively little potash as is shown by the following analysis of the soluble portion (96.20 per cent) of the salts.⁴

¹ From a brochure published in 1928 by the American Potash and Chemical Corporation.

² G. K. Gilbert, U. S. Geol. Survey Mon. 1, (1890).

³ G. F. Loughlin and G. R. Mansfield, U. S. Geol. Survey Bull. 795, 25-44 (1927).

⁴ H. S. Gale, *Eng. Mining J.*, 102, No. 18, p. 780 (1916).

	Per cent
K	0.07
Na	36.85
Ca	1.20
Mg	0.10
SO ₄	2.88
Cl	58.90
CO ₂	none
	<hr/> 100.00

The brine constitutes about one-fourth of the total volume of the salt beds, and the average composition is as follows:

	Grams per liter
Cl	192.0
K	10.6
Mg	6.3
SO ₄	5.2

Saline waters are also found throughout the desert within the clay. The composition of these brines, expressed in grams per liter, is shown in the following composite analysis:

Cl	96.15	Na	57.30
Br	0.00	K	2.94
I	0.00	Li	0.002
SO ₄	4.08	Ca	1.51
CO ₂	0.00	Sr	0.00
BO ₂	0.00	Mg	1.91

Sp. gr. at 25° C., 1.11.

Total solids at 180° C, 164.7 grams per liter.

The amount of potash available in this region is relatively small.

The Utah-Salduro Company started production of potassium salts from the brines of these salt beds in 1917; in 1920 it was the largest single producer in the United States. The plant was closed in 1921, and no potash production has been reported since that time.

Great Salt Lake.—Great Salt Lake, Utah, has a salinity of 20.35 per cent.¹ Of this salinity, only 3.16 per cent is potassium chloride while over 75 per cent is sodium chloride. The total supply of potash in the lake is large, but any exploitation of it for potash alone seems quite remote. In spite of difficulties two attempts were made during the war period, but very little information is at hand in regard to them.

¹ H. S. Gale, Potash in 1916, U. S. Geol. Survey.

Nebraska Lakes.—The sand hill region of Nebraska has many shallow lakes, whose waters range from fresh through all degrees of salinity, up to and exceeding 10 per cent. The depth of these lakes seldom exceeds 5 feet, and they vary in area from mere ponds to 600 acres. Over 100 of these lakes, scattered over an area of 800 square miles, contain sufficient potassium to be of some importance. Their aggregate area is over 6,000 acres. The lake bottoms are usually impervious sand, below which there is a sub-surface body of salts which rests on a second impervious stratum. These sub-surface salts may or may not contain commercial brines. Water occurring below the potash beds is usually fresh. W. B. Hicks¹ has reported on 101 of these lakes. He estimates that 215,000 short tons of K_2O are available in them and in underlying brines. Other lakes and various weakly alkaline waters may contribute a few hundred thousand tons in addition.

The commercial potash brines of these lakes vary both in salinity and in composition of the dissolved salts. Analyses of three of these lakes, as reported by Hicks, are given in Table V.

TABLE V.—COMPOSITION OF PRODUCTIVE POTASH BRINES IN NEBRASKA.

	Alkali Lake	Jesse Lake	Plant Lake
	Per cent	Per cent	Per cent
K	12.89	23.40	21.93
Na	28.33	20.74	21.77
Cl	2.36	3.71	2.36
SO ₄	4.72	14.84	12.44
CO ₃	30.33	26.52	28.39
HCO ₃	21.37	10.69	13.07
SiO ₂	—	.10	.04
Salinity	2.67	4.49	7.12
Specific gravity (25° C.)	1.022	1.038	1.062

About 25 plants were erected in this region during the war period; in 1918 they produced 116,000 tons of salts, equivalent to 29,000 tons of potash. The only processing necessary was the evaporation of the brines and drying of the salts, which were then ground and shipped to market. No production has been reported from this source in recent years.

Texas Lakes.—The brines from certain small and scattered alkali lakes in Gaines, Lynn and Terry Counties, Texas, contain potash and bromine² in workable quantities. The sands of the lake bottoms are impregnated to a depth of 5-20 feet with a brine consisting essentially of chlorides of

¹ U. S. Geol. Survey Bull., **715-I**, p. 125-39 (1921).

² *Amer. Fertilizer*, **52**, No. 8, 72-73 (1920).

sodium, magnesium and potassium. No estimate of available tonnage has been noted.

Deep Springs Valley.—In Deep Springs Valley, California, there exists a "salt marsh" or dry "lake" which contains a crystal body about $1\frac{1}{2}$ square miles in extent. This salt body contains a potash-bearing brine with an 8 per cent potassium chloride content.¹

Tonopah, Nevada.—A deposit containing about 1,000,000 tons of free sulfur and potash alum occurs about 35 miles west of Tonopah, Nevada. The alum and sulfur occur together in thin stringers throughout a mass of decomposed rhyolitic tuffs. L. Duncan² gives an analysis of the run-of-mine ore as follows:

TABLE VI.—ANALYSIS OF RUN-OF-MINE ORE.

	Per cent
$K_2Al_2(SO_4)_4 \cdot 24H_2O$	20.0
S (free)	15.0
SiO_2	58.8
Al_2O_3	2.6
$CaSO_4$	2.1
$CaCO_3$	1.2
Fe_2O_3	0.3
	<hr/> 100.0

Although the potash alum and sulfur are recoverable by simple methods, this deposit is of minor importance from a potash standpoint because alum contains only about 10 per cent K_2O , and the alum is only 20 per cent of the ore, a circumstance that makes the total K_2O reserves, as based on Duncan's figures, only 20,000 tons.

Sea and Ocean Waters.—Ocean water has seldom been considered seriously as a source of potash except as a by-product, although it contains potassium compounds. The cost of evaporation to recover a constituent present in such low concentration would be prohibitive. It is entirely possible, however, that various proposals to use solar evaporation to recover other valuable products in addition to potash might succeed. The salt-gardens at Giraud en Carquet at the mouth of the Rhone produced 80 per cent potassium chloride until operations were begun at Stassfurt. Solar refineries manufacturing salt from sea water³ and the brines of saline lakes can produce a low-grade potassium chloride from the bittern

¹ L. A. Palmer, *Chem. Met. Eng.*, **26**, 1034-1036 (1922) has discussed this deposit and methods of working it.

² *Chem. Met. Eng.*, **24**, 529 (1921).

³ Joel H. Hildebrand, *Ind. Eng. Chem.*, **10**, 96-105 (1918).

remaining after separating sodium chloride. The saline lakes as a source of potash are considered elsewhere.

Table VII, compiled by Enrico Niccoli, shows the composition of solids from various open and closed seas.

TABLE VII.—COMPOSITION OF SOLIDS IN OPEN AND CLOSED SEAS.*

	Caspian Sea	Black Sea	North Sea	Mediterranean Sea	Atlantic Ocean	Dead Sea
Total salts (per cent)	0.63	1.77	3.31	3.37	3.63	22.30
NaCl	58.25	77.39	78.04	77.07	77.03	36.55
KCl	1.27	1.07	2.09	2.48	3.89	4.57
CaCl ₂		0.20				11.38
MgCl ₂	10.00	7.38	8.81	8.76	7.86	45.20
NaBr + MgBr.		0.03	0.28	0.40	1.30	0.85
CaSO ₄	7.78	0.60	3.82	2.76	4.64	0.45
MgSO ₄	19.68	8.32	6.58	8.34	5.29	
CaCO ₃ + MgCO ₃	3.02	3.21	0.18	0.10		
	100.00	98.21	99.80	100.00	100.01	99.00

* Percentage of total salts.

Hildebrand states that the salt works around San Francisco Bay could produce about 2,800 tons of by-product potassium chloride for each 100,000 tons of sodium chloride produced. Thus, in a national emergency, sea water bitterns may take on some importance.

INSOLUBLE POTASH MINERALS

Because the insoluble potash minerals contain the country's greatest reserves of potash, they have been studied extensively and processes have been developed which would make it possible to produce potash from them should other sources of supply be cut off. Further study of these minerals is at present in progress in government laboratories.

Feldspar.—The feldspars are alkali or alkaline earth aluminum silicates, in which the base may be potassium, sodium, calcium or barium. The two important potash feldspars are orthoclase and microcline. The composition of both is expressed by the formula KAISi_3O_8 , their hardness is 6-6.5 and their specific gravity 2.54-2.56. Their theoretical composition is silica, 64.7 per cent; alumina, 18.4 per cent; and potash, 16.9 per cent. Sodium may partially or completely replace the potassium in these minerals. If the sodium predominates, the feldspar is called anorthoclase. As taken from the quarry good potash feldspar averages 10-12 per cent potash.

Potash feldspars are widely distributed,¹ and they may usually be mined by open pit methods. The mineral is hard, consolidated and difficult to quarry. Before any chemical treatment is applied the mineral must be ground, in marked contrast to greensand, which may be mined with a steam shovel and is fine enough for direct chemical treatment. The feldspar deposits of this country contain a tremendous amount of potash.

Processes for recovery of potash from feldspar.—Owing to its relatively high potash content, as compared with other potash silicates, and to its wide distribution, feldspar has received much attention and study. Although the extraction of potash from feldspar is a fairly simple matter from the chemist's viewpoint, this rock has not been successfully exploited as a source of potassium compounds, owing to the failure of producing potash cheaply enough to compete with the imported salts. It is unlikely that any process will succeed unless it makes provision for by-products to carry part of the cost of production. Processes for extracting potash from feldspar may be grouped into three divisions:

(1) Those that render the potash soluble by reaction with a salt, *e. g.*, calcium chloride.

(2) Those that use a base, such as lime, to break down the silicate. They include wet extraction after a lime treatment and volatilization by roasting the lime-feldspar mixture.

(3) Those specifying the use of acids.

Examples of each process will be considered briefly.

(1) *Treatment with salts.*—A. S. Cushman and his coworkers investigated the feldspar question and devised an interesting process.² A mixture of burned lime, calcium chloride and feldspar is formed into pellets about one-fourth inch in diameter, and these pellets are passed through a rotary kiln heated by oil or powdered coal. The calcium chloride reacts with the potassium compounds and renders the potash soluble. The red hot lumps fall into water as they leave the kiln, and the potassium chloride goes into solution. When the solution becomes sufficiently concentrated it is evaporated by being sprayed through the hot gases coming from the kiln. The very strong liquors resulting are finally dried in a rotary kiln, and the material is ready for market after it is ground. The product runs 70-80 per cent potassium chloride and 14-16 per cent sodium chloride, with some calcium compounds and water.

¹ F. S. Bastin, U. S. Geol. Survey Bull. 420.

² Cushman and Coggeshall, *Ind. Eng. Chem.*, 7, 145-151 (1915). Earlier papers are: *J. Am. Chem. Soc.*, 30, 779 (1908); U. S. Dept. Agr., Office of Public Roads Bull. No. 28 (1907); *Ind. Eng. Chem.*, 4, 821-827 (1912).

McClenahan¹ treats finely ground feldspar with ammonium bifluoride in a water solution. Decomposition of the rock results with the formation of a solution of ammonium silicofluoride, insoluble potassium silicofluoride and ammonium aluminofluoride. The solids are separated by decantation, washed and treated in steam at 650° F., which drives off the last of the silica as volatile ammonium silicofluoride. The alumina becomes partly potassium aluminofluoride and partly the hydrate. The potash and alumina are dissolved out of this mixture with lime and caustic alkali, and a residue of the calcium fluoride and insoluble materials present in the ore is left. Hydrofluoric acid is regenerated from the calcium fluoride by sulfuric acid. The caustic solution is treated with carbon dioxide, which precipitates the alumina and converts the potassium into the carbonate. The first mother liquor, to which has been added the additional ammonium silicofluoride volatilized from the potassium silicofluoride and ammonium aluminofluoride, is now treated with ammonia to precipitate the silica. The filtrate is evaporated to dryness, and the ammonia is driven off and used to regenerate the original reagent, ammonium bifluoride.

The process thus yields a pure alumina, potassium carbonate, which may contain a little sodium and amorphous, finely divided silica of high purity. The reagents are used cyclically.² The process utilizes every constituent of the original ore.

(2) *Reaction with a base.*—W. H. Ross³ found that when 1 part of feldspar and 1.7 parts of lime are digested with water at pressures of 10-15 atmospheres, 90 per cent of the potash passes into solution as the hydroxide; raising the pressure to 90 atmospheres results in almost total decomposition of the feldspar. The residue has the composition required for Portland cement clinker. In the absence of lime, no decomposition of the feldspar takes place even at 1,450 atmospheres. The Ross process is essentially the same as that applied later to greensand by the Eastern Potash Corporation.

One recent suggestion is interesting.⁴ Potash silicates may be substituted for sand in the volatilization of phosphorus from phosphate rock.

¹ U. S. Patents 1,426,890 and 1,426,891.

² Turrentine, Potash, p. 99.

³ *J. Ind. Eng. Chem.*, **9**, 467 (1917).

⁴ Ross, Mehring and Jones, *Ind. Eng. Chem.*, **16**, 563 (1924).

About 90 per cent of both the potash and phosphorus is volatilized. The volatilization of the potash is apparently brought about by the action of the free lime resulting from the decomposition of the phosphate rock. The recovered product, which consists of a solution of potassium phosphate in phosphoric acid, is a good starting material for the manufacture of concentrated fertilizers.

(3) *Acid extraction*.—C. A. Doremus invented a process for the recovery of alumina from bauxite and other aluminum compounds, including potassium aluminum silicates. When this process is applied to feldspar, 20 parts of the finely ground rock are treated with about 130 parts (as indicated by analysis) of 20 per cent hydrofluoric acid. The alumina goes into solution as fluoride, and the insoluble potassium silicofluoride that forms is removed by decantation or filtration. Any silica present in excess of that required to combine with the potash as the silicofluoride is precipitated, provided there are enough bases present to combine with both the hydrofluoric acid and the hydrofluosilicic acid. Aluminum fluoride is crystallized from the mother liquor and then heated in the presence of steam to form aluminum oxide and hydrofluoric acid, which is recovered and used again. The potassium fluosilicate may be treated with sulfuric acid to make hydrofluosilicic acid and potassium sulfate. Hydrofluoric acid may be regenerated from the former. In an alternative process the potassium silicofluoride may be heated with calcium sulfate to produce potassium sulfate and calcium fluoride.

Alunite.—Alunite is a hydrous sulfate of potassium and aluminum of hardness 3.5-4 and sp. gr. 2.58-2.72. As mined alunite is colorless or white to pink. It occurs in lenses, dikes or massive veins, and is a hard, consolidated mineral. The composition of alunite is expressed by the formula $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$, and its theoretical composition is therefore K_2O , 11.36 per cent; Al_2O_3 , 36.97 per cent; SO_3 , 38.63 per cent; and water of constitution, 13.04 per cent. Alunite is frequently associated with gold, the search for which has been responsible for uncovering many deposits in this country. Alunite deposits at Tolfa, Italy, have been worked since the 13th century, mainly for the production of alum. Like most minerals, alunite can seldom be mined in a pure state. The following table gives analyses of alunite from various sources in the United States:

TABLE VIII.—ANALYSES OF ALUNITE.

	1	2	3	4
	Per cent	Per cent	Per cent	Per cent
Al ₂ O ₃	39.03	38	37.18	34.40
Fe ₂ O ₃			Trace	Trace
SO ₄	38.93	38	38.34	36.54
P ₂ O ₅			0.58	0.50
K ₂ O	4.26	3	10.46	9.71
Na ₂ O	4.41	6	0.33	0.56
H ₂ O+	13.35		12.90	13.08
H ₂ O—			0.09	0.11
SiO ₂			0.22	5.28
Insoluble	0.50			
	100.48	---	100.10	100.18

No. 1, alunite from Red Mountain, Colo. E. B. Hurlbut, *Am. J. Sci.*, 3rd Ser., **48**, 130-131 (1894).

No. 2, alunite from Bovard District, Nevada. F. C. Shrader, *Econ. Geol.*, **8**, 763 (1913).

No. 3, Selected specimen of clear pink alunite from Marysvale, Utah District. B. S. Butler and H. S. Gale, U. S. Geol. Survey Bull. **511**, p. 8 (1912).

No. 4, Selected sample of light pink rock, same source as No. 3.

Large deposits of alunite are reported from Vancouver, B. C.,¹ Tolfa, Italy,² New South Wales,³ and from several states in the United States.^{2,4,5} Minor deposits are reported from many localities. The deposits of chief importance in this country are those in the Tushar Mountains of southern Utah, Pinto County, near Marysvale, about 200 miles south of Salt Lake City. Available estimates of possible potash tonnage from alunite are limited to one or two localities. As a source of potash, alunite does not have the great possibilities of heavy tonnage that feldspar or greensand possesses. Unfortunately the alunite deposits of the United States are located in the Far West, remote from the fertilizer markets of the East. Alunite is a potential source of aluminum as well as of potash, and this fact increases its importance.

Potash from alunite.—The chemistry of alunite has been described by a number of writers.⁶ Untreated alunite is insoluble in water, but when roasted at about 800° C. the water is evolved and the potassium becomes soluble as potassium sulfate. The aluminum appears as insoluble alu-

¹ *Oil, Paint Drug Repr.*, **89**, No. 27, 24 (1916).

² B. S. Butler and H. S. Gale, U. S. Geol. Survey Bull. **511**.

³ E. P. Pittman, Rpt. Geol. Survey, New South Wales, 1901, pp. 419-429.

⁴ G. F. Loughlin, U. S. Geol. Survey Bull. **620**.

⁵ E. S. Larsen, U. S. Geol. Survey Bull. **530**.

⁶ H. Bowley, *J. Proc. Roy. Soc., W. Australia*, **7**, 48-63 (1920-1).

E. S. Simpson, *Chem. Eng. Mining Rev. (Australia)*, **11**, 297-8 (1919).

F. E. James, Bull. Commonwealth, Australia Advisory Council, *Sci. & Ind.*, No. 3, (1917).

W. H. Waggaman and J. A. Cullen, U. S. Dept. Agr. Bull. **415** (1916).

minum oxide, and part of the oxides of sulfur is driven off. It is evident then that the potassium and aluminum can be separated by simple roasting and water extraction, and this property of alunite plays a prominent part in nearly all the processes proposed for its utilization.

Great interest was shown in alunite during the World War.¹ Many processes were proposed, and some actual operations were started. Several investigators planned to roast the alunite and leach out potassium sulfate; others added sulfuric acid to satisfy the aluminum and recovered alum and aluminum sulfate. Many of the patentees were primarily interested in potassium; others were interested in alumina, a few in sulfuric acid and some make provision for the production of all three. Several patents propose the production of alkali aluminate and its further processing. In addition to sulfuric acid as a reagent, hydrochloric and nitric acids, sodium chloride, calcium chloride and calcium carbonate are proposed. It is apparent that alunite has received its share of attention from investigators and inventors, and exploitation would follow swiftly should suitable market conditions arise. Mention should be made of the fact that both treated and roasted alunite are of some value when applied directly as fertilizer, and that roasted alunite gives quicker results.²

Alunite is being worked in a small way in Australia. Japanese alunite was mined to the extent of 19,255 tons in 1923. The production had fallen to 113 tons in 1925. No figures are available since that date. In 1927, 800 tons of alunite was mined in Italy. The deposits at Tolfa, estimated to contain 150-200 thousand tons of ore,³ have been worked since the thirteenth century, mainly for the production of alum. The industry is still active.

Leucite.—The term *leucite*, used in connection with potash, generally refers to leucite-bearing rocks, recent lavas, which, in this country at least, always contain other potash minerals. Rocks rich in leucite are known in only three localities in the United States. Two of these, located in the Bearpaw and Highwood Mountains in Montana,⁴ contain comparatively little potash, but the third, the Leucite Hills of Wyoming, has been estimated to contain 200,000,000 tons of K_2O , and an equal

¹ For a description of an alunite plant, see R. H. Tingley, *Rock Products*, **25**, No. 6, 38 (1922).

² W. H. Waggaman, U. S. Dept. Agr. Bur. Soils Cir. **70**, (1912).

³ H. M. Hoar, *loc. cit.*, p. 68.

⁴ Weed and Pirsson, *Am. J. Sci.*, 4th ser., **2**, 147 (1896). See also Pirsson, U. S. Geol. Survey Bull. **237** (1905).

quantity of alumina.¹ These hills are therefore a potash source of vast potential importance. Their remoteness from the market, however, and the difficulties of extracting the potash will probably postpone any large-scale exploitation for some time.

The leucite lavas of the Leucite Hills are wyomingite and orendite. They are fine grained, earthy appearing rocks. Ordinarily mica is the only mineral in them that can be recognized with the unaided eye. The mineralogical composition of wyomingite from Boar's Tusk, Leucite Hills is given by Schultz and Cross as—

	Per cent
Uncombined silica	18.7
Leucite (KAlSi_3O_8)	26.1
Noselite ($\text{Al}_2\text{Na}_5\text{SSi}_3\text{O}_{18}$)	8.7
Diopside ($\text{CaMgSi}_2\text{O}_6$)	18.8
Phlogopite ($\text{AlMg}_3\text{KH}_2\text{Si}_3\text{O}_{12}$)	19.9
Accessory minerals	7.8
	<hr/> 100.0

When the rock contains both leucite and sanidine (KAlSi_3O_8) in notable amount it is called orendite. The chemical composition of the potash-bearing minerals of the leucite rocks and of wyomingite and orendite from Zirkel Mesa, Leucite Hills, is given in Table IX.

TABLE IX.—COMPOSITION OF LEUCITE ROCKS AND ASSOCIATED MINERALS.*

	Leucite†	Sanidine†	Diopside	Phlogopite	Wyomingite	Orendite
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Silica (SiO_2)	55.0	64.7	50.86	42.56	53.70	54.08
Titanic acid (TiO_2)			3.03	2.09	1.92	2.08
Alumina (Al_2O_3)	23.5	18.4		12.18	11.16	9.49
Chromic oxide (Cr_2O_3)				0.73		
Ferric oxide (Fe_2O_3)			1.19	2.73	3.10	3.19
Ferrous oxide (FeO)			1.82	0.90	1.21	1.03
Magnesia (MgO)			17.42	22.40	6.44	6.74
Baryta (BaO)				1.00		
Lime (CaO)			23.23	0.20	3.46	3.55
Soda (Na_2O)			0.76	0.44	1.67	1.39
Potash (K_2O)	21.5	16.9	0.42	10.70	11.16	11.76
Water (H_2O)			0.31	2.35	3.41	3.50
Phosphoric acid (P_2O_5)					1.75	1.35
Sulfur trioxide (SO_3)					0.06	0.29
Fluorine (F)				2.46	0.44	0.49
Other constituents			0.03	0.06	0.92	1.03
Specific gravity					2.627	2.686

* Collected from Schultz and Cross, *loc. cit.*, p. 11-13.

† Theoretical composition.

¹ Schultz and Cross, U. S. Geol. Survey Bull. 512, p. 35.

The Leucite Hills rise abruptly from the surrounding plain and present extensive vertical rock faces, a situation that should make quarrying easy. The extraction of all the potash from these rocks involves the decomposition of at least three minerals—leucite, phlogopite and sanidine. Since all these minerals are silicates, sanidine itself being a variety of orthoclase, it would appear that any process successful with feldspar would also succeed with leucite rocks. The Sterling process, in which the ground rock is mixed with sodium chloride and fused in rotary kilns and the potash is volatilized and collected in bag filters, was developed to the point of large-scale production before the end of the period of high-priced potash. It would seem that the successful development of the Italian leucites¹ should point the way for investigators in this country, although the Italian problem differs in several aspects. Concentrating the leucite by electromagnetic means has been successful abroad and might succeed here, but it is unlikely that any process yielding potash alone will succeed in America under present conditions. The literature on the Italian leucite is very extensive. No production in the United States has been reported in recent years.

Italian leucite.—The Italian leucite deposits represent a potash reserve of tremendous importance. H. S. Washington² has described these deposits exhaustively. He estimates that they contain 8,786,200,000 metric tons of K_2O . According to J. W. Hinckley,³ “supplies to meet the world’s demands for potash over a period of 500 years are at present available and visible in these lavas at a cost not greater than that of the potash obtained from the Stassfurt deposits.” The chemistry of leucite has been thoroughly studied, workable processes for its treatment have been devised, and an industry based on it has been established in recent years. Although the annual output fluctuates (18,000 tons of potassium oxide in 1925 compared with 4,500 tons in 1927) the industry appears to be firmly established.

Greensand.—The term greensand or greensand marl refers to deposits, usually unconsolidated, of glauconite granules more or less contaminated with other minerals but frequently nearly 100 per cent glauconite. Greensand is very widely distributed; the most extensive deposits, however, are the beds of New Jersey. From the viewpoint of actual potash contained, these deposits are second in importance only to the Italian leucites.

¹ Carnevali, *Rass. min. met. chim.*, **66**, 802 (1927).

² *Met. Chem. Eng.*, **18**, 65-71 (1918).

³ *Chem. Trade J.*, **73**, 608 (1923).

Washington¹ estimates that the New Jersey beds contain 2,242,100,000 short tons of K_2O and that there is enough potash within reach of the steam shovel to last the United States a thousand years. G. R. Mansfield gives a splendid survey of these deposits.² The potash of greensand occurs in the glauconite.

Glauconite is a definite mineral that occurs in the rocks of nearly all geological ages from the Cambrian down to the most recent and is at present being formed on the bed of the ocean, although not all glauconite is of such origin. It is a granular, green to black, unconsolidated mineral of hardness³ two and specific gravity of 2.29-2.35. It is usually amorphous, although occasional crude crystals have been found. The chemical nature of glauconite is still in dispute. It is essentially a hydrous silicate of iron and potassium in which some of the iron is replaced by aluminum and other bases may replace part of the potassium.

The composition of glauconite is extremely variable with the exception of the silica, which is always very close to 50 per cent of the total. The apparent variable composition of glauconite is thought by some to be due to the extreme difficulty of securing a pure sample. The following analyses compiled by Mansfield will show what composition may be expected.

TABLE X.—CHEMICAL COMPOSITION OF GLAUCONITE FROM OLDER SEDIMENTARY DEPOSITS.

	1	2	3	4
	Per cent	Per cent	Per cent	Per cent
SiO_2	50.58	49.47	49.00	51.24
Fe_2O_3	19.50	19.46	10.56	13.44
FeO	2.06	3.36	3.06	3.06
Al_2O_3	6.72	5.59	15.21	12.22
CaO	.34	.60	.55	.10
MgO	4.10	3.96	2.65	3.93
K_2O	8.26	8.04	6.05	7.50
Na_2O	.04	.16	1.21	.31
CO_2	.30	.56	—	—
P_2O_5	.27	1.06	—	—
H_2O	7.76	8.54	11.64	8.20
	100.83	100.80	100.02	100.00

1. From Sewell, N. J.
2. Elmwood Road, N. J.
3. Ashgrove, near Elgin, Scotland.
4. Ontika, Russia.

¹ *Loc. cit.*, p. 17.

² U. S. Geol. Survey Bull. **737** (1922).

³ J. D. Dana, *System of Mineralogy*.

Greensand marl was extensively used directly as a fertilizer in the regions where it occurs as early as 100 years ago. The quantity used annually in the late sixties was nearly a million tons.¹ Of historical interest in this connection is an analysis of green earth (probably greensand) from Rancocas Creek, New Jersey, by Henry Seybert² in 1822. The potash in greensand becomes slowly available although the water-soluble potash is very low.³

The patent literature of greensand is very extensive. Some of the outstanding processes will be considered briefly.

Autoclaving with lime and steam.—The Eastern Potash Corporation, after successful small-scale experiments, started the construction of a large plant (1000 tons of greensand used daily) near New Brunswick, N. J., but the work was stopped owing to the falling potash prices at the close of the war. The process⁴ consisted in autoclaving greensand with lime and steam at about 470° C. to render the potassium soluble as potassium hydroxide. A high-grade sand lime brick was to be produced from the residue.

Roasting with salt and lime.—The processes of F. Tschirner⁵ formed the basis of the operations of the R. S. Ryan Company, which constructed and operated a successful pilot plant during the World War and laid plans for a commercial unit. Engineering estimates based on potash alone gave a very favorable outlook. A mixture of 10 parts of greensand, 12 parts of limesand and 3.5 parts of sodium chloride was heated in a rotary kiln at 800° C. The roasted mass was leached to dissolve out sodium and potassium chlorides, which were then separated by fractional crystallization. In the pilot plant about 80 per cent of the potash content of the greensand was recovered.

Acid extraction.—Greensand is readily attacked by mineral acids. The action of sulfuric acid is particularly interesting. The soluble constituents are removed by the acid, and a residue of practically pure silica remains. This silica was found by the Bureau of Soils⁶ to be an active adsorbent and decolorizing agent useful for decolorizing oils and for other purposes.

¹ G. H. Cook, *Geology of New Jersey*, p. 461 (1868).

² *Mem. Phila. Soc. Prom. Agr.*, **5**, 21 (1826).

³ *New Jersey Agr. Exp. Sta. Cir.*, **61** (1916).

⁴ R. N. Shreve, *Concrete* (Cement Mill ed.), **20**, 43-7; see also *Ind. Eng. Chem.*, **13**, 693-5 (1921).

⁵ U. S. Patents 1,254,450, 1,254,451 and 1,292,929.

⁶ Turrentine, Whittaker and Fox, *Ind. Eng. Chem.*, **17**, 1177 (1925), Whittaker and Fox, *Ibid.*, **19**, 467 (1927).

It was given the name "Glaucosil." Glaucosil appears to be the silica skeleton of the original glauconite granule, since it retains essentially the size and shape of the granule and does not go down to a mud as most minerals do when digested with acids. If the possibility of marketing the silica as a by-product is considered, the outlook for potash production from greensand is good. The alumina and iron present also offer opportunity for by-products.

The process consists in extracting the greensand with 40-60 per cent sulfuric acid and treating the liquors by any of several methods. Fractional crystallization to recover potash alum and iron sulfate may be used. Glaucosil is prepared from the insoluble residue by simply washing it free from acids and salts and drying.

The Moxham process¹ used by the Electro Co., of Odessa, Delaware, is also a sulfuric acid process. This company reported a small production in 1927.

Other processes.—It is difficult, or even impossible, to decide on the most important processes for greensand extraction, but those described have attracted more attention than others. Turrentine² gives a classification of the many processes that have been patented.

Shales and Slates.—The peculiar physical properties of slates and shales are quite familiar. Chemically the slates are extremely variable, and no formula can be assigned. They are not chemical individuals in the sense of alunite or orthoclase, but may be composed of consolidated mixtures of any of the common rock-forming minerals in varying stages of decomposition. The bulk of the material in slate appears to have been colloidal at the time of deposition, and under the microscope the optical properties shown are principally those of aggregates.³

The mining of slate for building and other purposes has long been an important industry, but it is only in the last few years that this rock has attracted any attention as a possible source of potash. In this connection the slates and shales of Georgia, Illinois and Minnesota are probably the most important, and of these, the slate of the Cartersville formation, Georgia, has attracted the most attention.

Georgia Shales.—This formation outcrops in a belt averaging one-half mile in width, extending through Cartersville and about 15 miles north-

¹ Turrentine, *Potash*, p. 111.

² *Ibid.*, p. 104.

³ For a discussion of the mineralogical composition of slates, see H. K. Shearer. *Geol. Survey of Georgia Bull.* 34.

east of that city. A thickness not exceeding 1000 feet is indicated.¹ Although no estimate of potash reserves in this region has been noted, by assuming a block of slate 15 miles by 0.5 mile by 1000 feet, running 170 lbs. of slate to the cubic foot and containing 8 per cent K_2O , a figure of 1,420,000,000 short tons of K_2O is obtained, an estimate that may be far in either direction from the truth, but which shows this deposit to be a vast potential source of potash.

A table showing the average of six analyses of Cartersville slate compiled by Shearer follows.

TABLE XI.—COMPOSITION OF CARTERSVILLE SLATE.

	Per cent
Silica (SiO_2)	56.73
Alumina (Al_2O_3)	19.27
Ferric oxide (Fe_2O_3)	5.57
Ferrous oxide (FeO)	1.80
Magnesia (MgO)	1.93
Lime (CaO)	.01
Soda (Na_2O)	.49
Potash (K_2O)	8.85
Loss on ignition	3.77
Moisture	.38
Carbon dioxide (CO_2)	.00
Titanium dioxide (TiO_2)	.88
	<hr/>
	99.77

Many of the processes for extracting potash from silicate rocks should be equally suitable for slate so far as the chemistry of the processes is concerned. Alumina appears here as a possible by-product as it does in the case of some other potash minerals. In general the slates are more easily mined than the feldspars, are less difficult to reduce to small size for chemical treatment, and are more readily attacked by reagents.

Probably the best means of obtaining potash from Georgia shale would be the utilization of the shale as a constituent of the raw mixture in the manufacture of cement (see p. 366), with the recovery of potash as a by-product.² The analyses show the one to three ratio of alumina to silica and low magnesia content essential to cement manufacture.

Shearer has described potash operations on Georgia shale up to 1918. Preliminary trials have indicated that the Doremus process (discussed under Feldspar) may be successfully applied to this material.

Illinois Shales.—Shales bearing 5-5.8 per cent of potash are reported from Union County and from Lee County, Illinois, but they differ con-

¹ Shearer, *loc. cit.*, p. 128-130.

² *Ibid.*, p. 116; Turrentine, *Potash*, p. 132.

siderably. In a study of these shales, M. M. Austin and S. W. Parr¹ find the potash of the Union County shale to be only 62 per cent recoverable with concentrated sulfuric acid and that from the Lee County shale only 15 per cent recoverable. Both of the shales have a composition that might be adapted to cement manufacture with a view to by-product potash, but direct potash production seems unlikely.

Minnesota Shales.—H. A. Schmitt² has described the Decorah and Galena formations near St. Paul. The potash content ranges from 5 to over 8 per cent, about 60 per cent of which is more easily available than the remainder. Schmitt has also described processes for utilization.

VEGETABLE OR ORGANIC SOURCES OF POTASH

Under this title are discussed vegetable and organic sources of potash with the exception of Steffen's waste, distillery waste, and wool scourings, which are considered under Potash from Industrial Waste. Kelp is particularly important. Some of the potash production described is the result of utilization of plant residues that are ordinarily waste material, but these sources are so characteristically vegetable that they seem to fall more properly in this section.

Potassium compounds are important constituents of nearly all plants, and theoretically, at least, potash could be produced from most plant residues. In the past crude potash has been produced in considerable amounts from wood and other plant ashes, and it is still so produced in some localities where wood is burned as fuel or where much wood or other plant waste is available. Obviously, the growing of any plant for the recovery of its potassium content would result in the rapid depletion of the soil and such an enterprise would be self-limiting. Seaweed would seem to be an exception because the potassium in the plants is supposed to be absorbed from the sea water and since the water around the plants is constantly changing, there would be little depletion of the source from which the plant draws its supply. In special cases the production of by-product potash from plant residues is still found profitable.

J. Fritsch³ gives the following analyses of a number of plants shown in Table XII.

¹ *Ind. Eng. Chem.*, **13**, 1144-1146 (1921).

² *Econ. Geol.*, **19**, 72-83 (1924).

³ *The Manufacture of Chemical Manures*, Translation by H. B. Stocks, 1920, p. 314.

TABLE XII.—POTASH CONTENT OF VARIOUS PLANTS.

Plant	Potash in 1000 parts	Plant	Potash in 1000 parts
Pine	0.45	Barley straw	5.80
Poplar	0.75	Fern	6.26
Beech	1.45	Reeds	7.22
Oak	1.53	Maize stalks	17.50
Willow	2.85	Sunflower stalks	20.00
Alder	3.90	Chrysanthemum	25.00
Wheat straw	3.90	Nettle	25.03
Thistles	5.00	Vetches (tares) stalks	27.50
Vine	5.50	Absinth stems	73.00
		Fumitory	79.00

Wood Ashes and Lime Kiln Ashes.—The ancient Greeks and Romans were familiar with the leaching of wood ashes for soluble alkali, but were unable to distinguish between potash and soda, both of which were known by the general name; nitrum.

Prior to the extensive exploitation of the Stassfurt salts, wood ashes were the chief source of potash salts. In fact, in the middle of the last century, $\frac{2}{3}$ - $\frac{3}{4}$ of the world's potash was produced in Canada from wood ashes. In 1851, there were 273 asheries in Canada, and in 1871 there were 519, but this number had dwindled to 128 by 1891. Canada exported 27,000,000 lbs. of potash in 1850.¹

Potash manufacture from wood ashes was a very important industry in colonial America during the latter part of the 18th century and in the United States until about the middle of the 19th century. The incentive of profit from potash stimulated the clearing of much land that otherwise would not have been cleared until a much later date. C. A. Browne² has written an interesting account of the early potash industry in the United States. Today wood ashes occupy a very minor position in the industry. According to H. J. Wheeler³ they may contain 2.5-12 per cent of potash, 30-35 per cent of calcium oxide, 3-4 per cent of magnesium oxide, and 1-2.5 per cent of phosphoric acid. In burning wood for recovery of its potassium content careful control of conditions is necessary. Too high a temperature may result in volatilization of potassium salts and formation of insoluble potassium silicates.⁴

Lime kiln ashes consist usually of a mixture of waste lime and wood and coal ashes and are of low potash content, ranging from 1 to 2 per cent. They have sometimes been used directly as a fertilizer.

¹ E. B. Biggar, *Trans. Am. Inst. Chem. Eng.*, **10**, 85-103; C. T. Edgar, *Met. Chem. Eng.*, **18**, 537-9 (1918).

² *J. Chem. Education*, **3**, 749-756 (1926).

³ *Manures and Fertilizers*, 1913, p. 228.

⁴ For a description of the preparation of potash salts from wood ashes, see J. W. Mellor, *Treatise on Inorganic and Theoretical Chemistry*, vol. **11**, p. 438; C. T. Edgar, *loc. cit.*

Flax Mill Refuse.—Flax mill¹ refuse contains about 0.7 per cent of K_2O and is used directly as fertilizer in New Zealand.

Hedge Clippings.—Ashes of hedge clippings contain 10-13 per cent of K_2O ² and are valuable if loss does not occur by exposing the ashes to rainfall.

Tobacco Stems.—Tobacco stems and waste midribs from the leaves, sold as tobacco stems, are reported by the Massachusetts Experiment Station to contain 3.76-8.22 per cent potash. They are rich also in nitrogen.

Corn Cobs.—The potash content of corn cobs is exceptionally high, averaging 6.8 per cent, while the ashes from them contain about 50 per cent of potash.³

Cottonseed Hulls.—The ashes from cottonseed hulls were formerly used extensively for growing tobacco in the Connecticut Valley. The Massachusetts Experiment Station found the potash content to range from 10 to 42 per cent, the average being 22.48 per cent. In addition, they contain 3-13 per cent of phosphoric acid, 9 per cent of lime and 10 per cent of magnesia.

Glacialo.—About 1850 a plant called glacialo (*Mesembryanthemum crystallineum*) was grown in Sardinia for the potash from its ashes. This ash contained about 30 per cent of potassium carbonate and 6 per cent of sodium carbonate.⁴

Caucasian Sunflower.—The sunflower grown in the Caucasus for its seed is particularly interesting and deserves more than passing mention. The stalks and branches are burned as a source of potash. The first factory for this purpose was established at Maikopp, by Schaponalow, in 1899. By 1907, 24 factories were producing a total of 700,000-900,000 poods with a value of 22,000,000 rubles. The pood is equivalent to 40 funt or 36.113 lbs. Advp. (16.38 kg.) A deciatine (2.70 acres, or 109.25 ares) of sunflower on good land yields 200-300 poods of stem, which in turn yield 3-5 per cent of ash. Three to four poods of ashes give a pood of potash. The analysis of sunflower potash from Kuban according to Fritsch gave water 1.7, potassium carbonate 89, sodium carbonate 5.0, potassium sulfate 2.01, potassium chloride 1.51, and insoluble matter 0.74 per cent. Three-fourths of the potash is exported to New York, London and Hamburg.

¹ C. Ashton, *J. Agr. New Zealand*, **14**, 440-7 (1917).

² E. J. Russell, *J. Board Agr.*, **21**, 694 (1914).

³ H. J. Wheeler, *loc. cit.*, p. 233.

⁴ J. Fritsch, *loc. cit.*, p. 295.

Kelp.—The burning of seaweed and spreading of the ashes therefrom on the land for fertilizer dates as early as the 18th century and perhaps earlier. Crofters on the shores of West Scotland, Ireland, Northwestern France, and Japan burned drift kelp for fuel and used the ashes very successfully as fertilizer with the result that at the beginning of the 19th century kelp harvesting was an important industry. The impure alkali carbonate known as barilla was obtained from ashes of seaweed by lixiviation and fractional crystallization. Most of the potash used in the industries and arts was obtained from barilla and kelp. The term kelp was then used frequently as meaning ashes of seaweed.

In 1911 the Congress of the United States authorized the Bureau of Soils and the Geological Survey to investigate the fertilizer resources of the United States, and under this authorization surveys of Pacific Coast kelps from Alaska to Mexico were made. The preliminary report of work under this authorization is in Sen. Doc. 190, 62nd Congress, 2nd Session, Fertilizer Resources of the United States, by F. K. Cameron, R. B. Moore and several others. The extensive survey referred to is contained chiefly in Report 100, Potash from Kelp, by F. K. Cameron, W. C. Crandall, Geo. B. Ribb and T. C. Frye.

These surveys disclosed the fact that vast quantities of potash could be produced annually from Pacific Coast kelps. The plant of chief importance is the giant kelp *Macrocystis pyrifera*.¹ In 1917 the Bureau of Soils constructed a small plant at Summerland, Calif., for the study of methods for the production of potash and other materials from kelp. The experiments were continued until 1921.

Briefly the process was as follows: The kelp was harvested, dried and subjected to destructive distillation, and the resulting mass was leached to remove its water-soluble constituents. The carbon residue was processed and converted into a very active bleaching agent. The water solution was evaporated, and iodine and potash salts were recovered. The carbon was the most important and became the main product; it was marketed under the name of Kelpchar and found wide application. The potash normally produced was 80 per cent potassium chloride. An analysis is given in Table XIII.

Ammonia and tar derivatives are also by-products of the process.

Other processes were developed, and several plants were constructed by private concerns. The Diamond Match Company produced high-

¹ Brandt and Turrentine, U. S. Dept. Agr. Bull. 1191.

TABLE XIII.—KELP POTASH, FERTILIZER GRADE.*

	Per cent
Potassium chloride	81.0
Sodium chloride	3.0
Sodium sulfate	9.2
Sodium carbonate	3.5
Water	2.5

* Turrentine, Potash, p. 57.

grade potassium chloride; the Swift Fertilizer Company prepared the thoroughly dried kelp to be used directly as fertilizer. The product contained 15 per cent of potassium oxide, and about 3 per cent of ammonia.

An important development was that of the Hercules Powder Company,¹ which in 1918 was cutting about three-fourths of all the kelp cut on the Pacific Coast, their average monthly cut in 1917 being 24,000 tons. The plant represents an investment of about \$5,000,000 and covers about 30 acres.

Special ocean-going harvesters were used. The kelp was macerated on the harvester itself and thereafter handled by pumps. The macerated kelp was allowed to ferment in wooden tanks for 10-14 days. In this fermentation organic acids—acetic, butyric, propionic, etc.—were formed and converted to their respective calcium salts by the addition of lime. These went into solution along with potassium salts and other compounds released in the breaking down of the kelp. After fermentation the liquor was screened and filtered. The solid matter was discarded, while the mother liquor, containing potassium and sodium chlorides and the calcium salts of fatty acids, was processed further. The calcium salts of the fatty acids and 95-98 per cent potassium chloride were recovered by evaporation and cooling.

In 1917 and 1918 the annual crop of kelp was about 400,000 tons exclusive of the large quantities grown in the Puget Sound and Alaska areas. Since raw kelp contains about 1.5 per cent of potassium oxide that produced annually from the 400,000 tons alone would be 6,000 tons.

Some interest in kelp has been shown in other lands. Industries based on it exist or have existed in Japan, Norway, England, Scotland and France. It has been made to yield a variety of products, including foods.²

Miscellaneous.—Residues from the manufacture of olive oil, almond shells, water, hyacinth roots, and banana skins have been considered as sources of potash.

¹ *Mct. Chem. Eng.*, **18**, 576-580 (1918).

² *J. Dept. Agr. Victoria*, **18**, 478 (1920); G. M. Ryson, *Chem. Age*, (London), **15**, 390-3 (1926); *Bull. Imperial Inst.*, **4**, 125 (1906); W. Singleton, *Ind. Chemist*, **3**, 267-270 (1927).

POTASH FROM INDUSTRIAL WASTES

Potash is present in many industrial wastes, and the recovery of such potash would go far toward making the United States independent of foreign sources. The presence of potash in a waste material, however, does not mean that it is feasible or profitable to recover it. Frequently the reverse is true. Nevertheless it is probable that much larger quantities could be recovered annually than are being recovered at present. Great interest was shown in this subject during the war period and much progress was made, but it was only natural that much of this interest would subside at the close of the war.

Potash from Cement Kilns.—Conditions prevailing in cement kilns are almost ideal for dust production. Powdered materials are tumbled about in the kiln while a high velocity gas stream passes over them. If this dust is allowed to escape it constitutes a nuisance which becomes a frequent cause of litigation. At the larger plants as much as 100 tons of dust a day may be blown into the atmosphere. Besides eliminating the nuisance the recovery of this dust represents a real saving.

It has long been known that cement dust contains potash. Ross, Merz and Wagner¹ made a thorough study of the possible production of potash as a by-product of cement manufacture and found that the raw mixture (consisting of limestone or other calcareous material mixed with clay, shale, blast-furnace slag or other argillo-silicious material) used in cement plants in America contained from 0.2 to 1.16 per cent potash, and that from 24.5 to 95.9 per cent of this was volatilized in the kiln and carried off by the gas stream to be lost with the dust unless means were taken to recover it. It was estimated that in 1917 about 90,000 tons of potash was escaping from cement mills annually.

The potash content of cement mill flue dust varies widely owing to fluctuation in the amount of potassium compounds in the raw mixture, the percentage of this potash volatilized, the amount of other dust that serves to dilute the potash, the method of firing the kiln, etc. In extreme cases the percentage of potash in the dust may be as low as 1.4 or as high as 35 per cent.

Potassium compounds occurring in cement dust differ widely in solubility. Considerably more than half of the potash is water soluble and is the portion that volatilizes and escapes from the mixture without recombining to form less soluble compounds in the cooler part of the kiln.

¹ U. S. Dept. Agr. Bull. 572 (1917).

It is chiefly potassium chloride and sulfate. Most of the remainder of the potash, which is slowly soluble in water and readily soluble in acids, is reported by Ross, Merz and Wagner¹ to consist of potassium silicates resulting from recombination of the potassium compounds with the silicious materials in the dust. The percentage of such potash is much lower in oil-fired than in coal-fired kilns. A small amount of the potash is insoluble and consists of potassium compounds from the raw mixture that have passed through the kiln without decomposition.

The method of potash recovery used at any particular cement plant will depend in general on the dust recovery system in use. Dust recovery methods may be roughly classified as wet, dry, and combinations of these.²

Wet methods, consisting of spray chambers or other means of bringing the dust-laden gases in contact with water, are sometimes favored when wet processes of concentrating the potash are to be used later. These methods may also be used in connection with a Cottrell electrical precipitator. The dry methods are usually combinations of settling chambers and electrical precipitators.

In some installations sufficient concentration of the potash to enable the producer to sell the product without further processing is obtained by fractional dust collection; in other cases further concentration is accomplished by wet methods (leaching, crystallization, etc.). Fox and Whittaker³ found that the potash in cement dust could be concentrated to a marked extent by air elutriation, the higher percentage of potash being present in those fractions containing the smaller particles.

Many suggestions have been made for increasing the potash content of the dust, but any method that would affect the quality of the cement or increase the cost of its production is, of course, not to be considered, since cement is the primary product. Two general methods have been proposed. The first, a chemical method, is usually effected by taking advantage of the higher volatility of potassium halides by adding to the raw mix a cheap reagent, *e. g.*, sodium chloride, which will displace the potassium as the halide. It is said that the quality of the cement is unaffected by such measures. The second method consists in choosing for the raw mix materials that bear a higher potash content. Georgia, Illinois and Minnesota shales, greensand, and feldspar have been suggested for this purpose.

¹ *Loc. cit.*

² For a more detailed discussion, see A. W. G. Wilson, Canada Dept. Mines, Mines Branch, Bull. **29** (1919); B. C. Karup, *Chem. Met. Eng.*, **25**, 316 (1921); J. G. Dean, *Ibid.*, **19**, 439 (1918); J. W. Turrentine, *Potash*, pp. 141-160.

³ *J. Ind. Eng. Chem.*, **16**, 1044 (1924).

And here again it appears that with proper precaution the quality of the cement would be unaffected. A combination of the two methods would probably result in the largest potash production.

In common with other potash sources, cement mill potash attracted considerable attention during the war period, both here and abroad. Wilson, writing in 1919, lists 15 cement plants in the United States as being equipped with potash recovery equipment. With the fall of the potash market, most of these plants suspended operation. The Bureau of Mines (Mineral Resources of the U. S.) reports no cement dust potash in either 1926 or 1927. The writers are informed that further research is in progress in Federal and private laboratories.

Potash from Blast Furnaces.—As is the case in the cement kiln, part of the potash that is contained in the raw materials that are used in the blast furnace is volatilized and carried out of the furnace by the gas stream to be deposited later with other dust in various parts of the equipment. Merz and Ross¹ have made a comprehensive survey of this problem.

The raw materials of the blast furnace industry consist of iron ore (limonite, hematite, magnetite, etc.), fuel (usually coke), and fluxes (consisting mainly of limestone or dolomite). The potash content of each of these, based on a weighted average, is about 0.2 per cent, which is less than one-third as great as the potash content of the raw mix in the cement industry. The percentage of potash in the ores ranges from 0.04 to over 2 per cent, but the consumption of high potash ores is relatively small. The total amount of potash in the ore, fuel and flux amounts, on the average, to 13.1 pounds per ton of pig iron; of this, 8.2 pounds is lost in the slag, and 4.9 pounds is carried over per ton of pig iron.

Merz and Ross estimated the loss of recoverable potash as 84,000 tons per annum, a figure that is probably low for present conditions and that could be greatly augmented if steps were taken to increase the proportion of the potash volatilized. K. M. Chance² found in the case of several British blast furnaces that adding salt in sufficient quantity to volatilize the potash always doubled the amount of potassium compounds found in the gas, and frequently trebled or quadrupled it.

Any general description of methods for collecting the dust and potash would follow in outline the methods used in the cement industry. It is a

¹ U. S. Dept. Agr. Bull. **1226** (1924).

² *J. Soc. Chem. Ind.*, **37**, 222 T, 88 A (1918).

problem of dust-settling chambers, spray systems, electrical precipitators and other gas-cleaning apparatus.¹

The blast furnace gases deposit their burden of dust in various parts of the plant in a manner governed by the velocity of the gas, size of the dust particles and other factors. This results in the potash being concentrated to some extent in places where conditions are right for its deposition.

As in the cement industry, many factors are involved. Since they differ with the locality and the particular plant, any prediction as to the future of potash from this source would be valueless, unless it were based on most careful surveys and investigation. In an emergency the blast furnaces of America could produce important amounts of potash, but whether the practice will become general in peace times remains to be seen. At least two furnaces are recovering potash at present.

Potash from Steffen's Waste.—In the crystallization of sugar from beet molasses, a point is reached where further production of sugar by simple crystallization is impractical although the sugar content of the molasses may still be as high as 50 per cent. The Steffen process is used to recover this sugar. Briefly, it consists in diluting the liquor and adding caustic lime; this results in the formation of calcium saccharate, which is removed by filtration. This first step is carried out in cold solutions and recovers only part of the sugar. The remainder of the sugar is recovered by treating the filtrate from the first step at a higher temperature. This gives a liquor that is practically sugar-free and is known as Steffen's waste. It contains about 90 per cent of the potassium present in the beet. The other 10 per cent remains in the pulp. The discharge of this waste into streams or sewer systems is objectionable, and its disposal becomes a problem.

TABLE XIV.—APPROXIMATE COMPOSITION OF STEFFEN'S WASTE WATER.*

	Per cent
Moisture	97.00
Dry substance	3.00
Carbonate ash	1.00
Sugar	0.30
Organic non-sugar	1.70
Nitrogen	0.16
Potash (K_2O)	0.35

* After carbonating and filtering to remove free lime.

¹ For further discussion, see Turrentine, Potash, pp. 129-140.

This waste liquor has a specific gravity of about 1.014 and contains about 3 per cent of solids, which consist of nitrogenous organic compounds, potassium and sodium compounds, and other bodies. The composition of Steffen's waste, as given by H. E. Zitkowski,¹ is shown in Table XIV.

Geldard and Chase² estimated the annual production of this waste water as 2,500,000 tons, which on the basis of the above analysis could be made to yield 8,700 tons of K_2O . J. B. C. Kershaw³ quotes an estimate of 12,000 tons of potash annually from Steffen's waste. Not all the beet sugar molasses is treated by the Steffen's process so that the total K_2O in the beet crop is much larger. Zitkowski, calculating on the basis of a 6,000,000 ton beet crop, estimated it as about 18,000 tons. About 40 per cent of the beet sugar molasses and most of the pulp is utilized for stock feed, so that about one-half (40 per cent plus the 10 per cent in the pulp) is at present finding its way back to the land, provided efficient use is being made of the farm manures. In addition, some manufacturers use their waste Steffen's liquor for irrigation purposes, thereby returning the potash to the land, but this is possible only in isolated cases and only about 8 per cent of the beet crop is so handled.

The development of a large potash industry based on Steffen's waste at present appears rather unlikely. Several processes for the utilization of this waste have been proposed, but they have been thoroughly treated by others⁴ and will not be discussed here.

In addition to potash, it is possible to produce a whole series of organic compounds, as well as ammonium sulfate, and thereby distribute the cost. In Germany, the Bueh processes of destructive distillation are applied to the waste liquor of the strontium process for desugarizing molasses, which is similar in principle to Steffen's process and by this means 5,000 tons of potassium cyanide and 5,000 tons of ammonium sulfate are produced annually, according to Zitkowski.

Potash from Wool Scourings.—Much of the potassium in plants eaten by sheep is exuded from the skin in an oily sweat called suint or yolk. Suint consists largely of potassium salts of organic acids mixed with fatty substances; it is taken up by the wool and may represent as much as one-third of its weight. Dioscorides, in the first century, referred to a mixture

¹ *J. Ind. Eng. Chem.*, **9**, 692-694 (1917).

² *Facts about Sugar*, **20**, 304-307 (1925).

³ *Ind. Chemist*, **1**, 545 (1925).

⁴ Zitkowski, *loc. cit.*; Geldard, *loc. cit.*; *Chem. Met. Eng.*, **30**, 394-397 (1924); **32**, 195-197 (1925). *Bur. Standards Cir.* **145** (1924), contains an exhaustive survey of the patent literature.

of water and wool fat, calling it oesypus. It was known by that name until the middle of the seventeenth century. Roman ladies regarded it as a choice cosmetic and N. Culpeper's *Pharmacopœia Londinensis* (London, 1653) lists it as a remedy. The modern preparation "Lanoline" is made from wool fat.

The first step in treating the raw wool is to wash or scour it thoroughly. The resulting liquors are very complex, containing, as they do, the natural wool fats and waxes, large quantities of dirt, animal exudations and excrement, and also the soaps and alkalies used in the scouring.¹ These liquors are capable of yielding a number of important products. Veitch and Benedict² have estimated that 30,000-35,000 tons of grease, 30,000-45,000 tons of dirt, 20,000-24,000 tons of potash salts and 7,500 tons of nitrogenous matter, expressed as dried albumen, are annually contained in the wool scouring waste liquors of this country.

Any successful process for the recovery of the potassium compounds that are now lost in wool scourings will be one which does not interfere with the proper cleaning of the wool and which will permit recovery of the other values present in the liquor. Veitch and Benedict also discussed several procedures, but it will be sufficient for present purposes to outline a method known as the steeping process, which has been used in England, France, Belgium and the United States.

The potash salts may be removed from the wool by steeping in cold water without greatly affecting the grease. This is done countercurrent fashion, so that the liquor moves in one direction and the wool in the other. When the concentration becomes high enough the liquor is evaporated to about one-tenth of its volume in triple-effect evaporators, and the resulting mass is incinerated in a reverberatory furnace. The product is a red-brown coke containing about 40 per cent of K_2O . It is used in making fertilizers, particularly when it is desirable that the potash be present as the carbonate. The partially cleaned wool is then scoured by one of the regular processes.

The future of potash production from this source is problematical. No production has been reported in recent years.

Potash as a By-Product of the Chilean Nitrate Industry.—The average potassium nitrate content of Chilean nitrate as shipped is approximately

¹ For a recent review of wool scouring and a 12 entry bibliography, see H. Wennström and C. P. Harris, *Oil and Fat Ind.*, 4, No. 10, 353-356 (1927).

² Unpublished paper read before the American Institute of Chemical Engineers at Providence, R. I. (1925).

2 per cent. For the year 1918, 30,000 tons of potash (K_2O) were contained in the Chilean product.¹

In the ordinary process of leaching the caliche (crude nitrate ore) the potassium nitrate becomes concentrated in the mother liquor, and it is comparatively easy to produce from this a "high potash nitrate;" this represents only a fraction of the total product, but it is sold at a premium. This "high potash nitrate" contains from 25 to 60 per cent potassium nitrate. Several plants are now producing high potash nitrates, the usual grade being a mixture of 65 per cent sodium nitrate and 30 per cent potassium nitrate.² It is thought that this product is marketed chiefly in the United States.

C. M. Barton³ estimates the amount of potash that could be produced annually from Chilean nitrate as 720,000 tons. Hoar states that should all the nitrate producers take up the work of potash recovery, the result would be an annual saving of 120,000 tons of actual potash, which could eventually be raised to 320,000 tons of potash (K_2O) as a by-product of the nitrate industry. The du Pont Company, according to Barton, has been able to produce 10,000 tons of 25 per cent potassium nitrate annually from caliche.

Potash from Distillery Waste.—In the manufacture of alcohol, molasses is fermented and then distilled. The residual liquor contains the potash and nitrogen originally present in the molasses. The dumping of this liquor into harbors and streams constitutes a serious nuisance, and for this reason its utilization for the production of by-products is particularly attractive. In at least one plant, that of the U. S. Industrial Chemical Company at Baltimore, Md., potash and ammonium sulfate are being produced from this liquor. The importance of the industry is evident from the fact that it ranks second only to Searles Lake as a producer of American potash. This company is now in its sixth year of production.

The process, as described by Turrentine, is briefly as follows: The waste liquor, after concentration by evaporation to the point where it will support its own combustion, is sprayed upward into a combustion chamber; here the remaining water is evaporated, and the solids are burned. The ash accumulates on the floor of the furnace, forming a sintered mass rich enough in potash to be marketed directly after grinding.

¹ P. F. Holstein, *J. Ind. Eng. Chem.*, **12**, 290-293 (1920).

² J. R. Faust, *Ibid.*, **19**, 276-7 (1927).

³ *Met. Chem. Eng.*, **18**, 248 (1918).

The hot gases from the furnace are passed through dust-settling chambers and then through waste-heat boilers. A further cleaning is effected by Cottrell precipitators, and finally by means of an absorption apparatus ammonia is recovered as the sulfate. Very thorough utilization of the distillery waste is thus obtained.

Table XV, showing the analysis of a composite sample of distillery-waste potash produced by the U. S. Industrial Chemical Company, is given by Turrentine.

TABLE XV.—COMPOSITION OF COMPOSITE SAMPLE OF DISTILLERY WASTE POTASH REPRESENTING 100 CARLOADS.

	Per cent
Moisture at 100° C.	0.17
Insoluble in acid before ignition	5.82
Iron and aluminum oxides (Fe_2O_3 , Al_2O_3)	6.40
Lime (CaO)	16.08
Magnesia (MgO)	4.80
Manganese oxide (MnO_2)	Trace
Potash (K_2O , sol. in dil. HCl)	34.72
Potash (K_2O , water soluble)	33.88
Total phosphoric acid (P_2O_5)	2.16
Insoluble phosphoric acid (P_2O_5)	0.47
Citrate soluble phosphoric acid (available P_2O_5)	1.69
Nitrogen (N)	0.30
Equivalent NH_3	0.36
Carbonate (as CO_2)	8.10
Total sulfur (as SO_3)	12.50
Chlorides (as Cl)	8.91

The future of potash from this source is of course dependent upon the future of alcohol. Turrentine has estimated that all the molasses from the sugar crop of the Americas is equivalent to 140,000 tons of potash annually.

THE POTASH INDUSTRY

In this section a brief statistical review of world production and consumption of potash is given.

The Domestic Industry.—The attempt to establish an American potash industry really dates from about 1911 and is largely the result of a potash controversy with the German interests. Surveys of various sources were inaugurated and are still being conducted. At the outset of the World War little had been done in the way of commercial exploitation, but tremendous activity immediately was aroused and practically all sources were utilized. Aside from a small wood ash potash industry, American

production dates from 1915, when 1,090 tons of pure potash was produced by five plants. Development thereafter was rapid. A summary of the industry from 1916 to 1929, inclusive, is given in Table XVI.

TABLE XVI.—POTASH PRODUCED AND SOLD IN THE UNITED STATES, 1916-1929.

	Number of plants		Production		
	Total	Exclusive of producers of wood ash potash	Crude potash	Available content of K ₂ O	Sales of K ₂ O
			Short tons	Short tons	Short tons
1916	70	25	35,739	9,720	9,720
1917	95	46	126,961	32,573	32,573
1918	128	77	207,686	54,803	38,580
1919	102	67	116,634	32,474	45,728
1920	66	40	166,834	48,077	41,444
1921	20	19	25,485	10,171	4,408
1922	12	12	25,176	11,714	11,313
1923	12	12	30,020	20,215	19,281
1924	11	11	43,734	22,903	21,880
1925	9	9	51,565	25,448	25,802
1926	7	7	46,324	23,366	25,660
1927	9	9	76,819	43,510	49,500
1928			104,129	59,910	60,370
1929			107,820	61,590	57,540

Exportation of potash from the United States is practically negligible, the gross shipments being 1,965 short tons for 1927. Imports for 1927, arranged by materials, is shown in Table XVII. In Table XVIII the distribution by countries and materials for 1927 is given.

TABLE XVII.—POTASH MATERIALS IMPORTED FOR CONSUMPTION IN THE UNITED STATES—1927

Materials	Approximate K ₂ O content	Short tons	K ₂ O content	
			Short tons	Percentage of total
	Per cent			
Kainite	12.4	115,345	14,303	6.3
Manure salts	20.0	311,357	62,271	27.7
Muriate (chloride)	50.0	183,475	91,738	40.8
Sulfate	48.6	77,172	37,506	16.7
		687,349	205,818	91.5
Miscellaneous potassium salts used in chemical industries*		43,249	19,155	8.5
		730,597	224,973	100.0

* Including 4,826 tons of crude nitrate, part of which probably was used as fertilizer.

All other potassium compounds, used chiefly in chemical industries, amounted to 38,349 short tons of crude salts or 17,440 short tons of K₂O. The total consumption in the United States for 1927 was 825,319 tons of material containing 274,437 tons of K₂O. Eleven per cent of this ma-

terial, containing 18 per cent of the K_2O , was produced in the United States. All but approximately 5 per cent was used in the manufacture of fertilizers.

TABLE XVIII.—POTASH FERTILIZER MATERIALS IMPORTED INTO THE UNITED STATES IN 1927 (SHORT TONS) AND COUNTRIES SHIPPING.

Country	Muriate (Chloride)	Sulfate	Manure salts	Kainite	Nitrate*
Belgium	42,213	5,948	99,393	20,875	
Canada	1,839	142			
Chile					4,460
France	18,915	1,818	10,762	12,778	66
Germany	108,632	66,815	195,579	80,708	144
Hong Kong	1	1			
India (British)					56
Netherlands	2,594	2,448	5,624	984	100
Spain	9,281				
	185,475	77,172	311,358	115,345	4,826
K_2O content	91,738	37,506	62,272	14,303	1,930

* Crude saltpeter, used principally by the chemical industries.

The Foreign Industry.—Germany has led the world in potash production since the beginning of operations at Stassfurt and maintains that leadership today in spite of recent developments in other countries. Of the world's production of potash minerals, Germany produced 80 per cent in 1925 and 77 per cent in 1927. France produced 16 per cent in 1925 and 19 per cent in 1927. These figures are on a K_2O basis. The third largest producer is Poland with the United States ranking fourth, but each of the latter two nations produces only about 2 per cent of the world's total production of K_2O . The data for Spain for 1927 are not available but her production was less than that of the United States for 1926, being less than 1 per cent of the world's total (K_2O basis).

Table XIX will show in more detail the distribution of the world's production of potash in recent years. The last normal year before the war (1913) is included.

ANALYTICAL PROCESSES

The determination of potassium has received the attention of many chemists. The literature is very extensive and many methods are available. The choice of method should be governed by several factors, among which are (1) the nature of the material to be analyzed, (2) the accuracy desired, (3) the speed required, and (4) the cost of the reagents. This

TABLE XIX.—WORLD'S PRODUCTION OF POTASH MINERALS AND CONTENT OF K₂O, 1913 AND 1925-29.
(Metric Tons)

Country and mineral	1913		1925		1928		1929	
	Output	K ₂ O content	Output	K ₂ O content	Output	K ₂ O content	Output	K ₂ O content
Australia, New South Wales, Alunite	2,271	*	540 336	45 *	*	*	*	*
China§								
Ethiopia, crude salts								
France (Alsace) crude salts								
Germany (crude salts)	†		1,926,346	311,892†	1,300	650	*	*
India (British) nitrate of potash	11,956,528	*	12,020,576	1,574,839	2,580,196	410,035†	*	*
Italy:	14,694	*	6,450§	2,580	12,489,070	2,691,128	3,124,816	493,934
Alunite					4,800	2,000	*	*
Leucite Rock	5,976	*	1,500	*	195	20	210	22
Japan, alunite	1,600	*	226,000	18,000	39,200	3,200	*	*
Poland:			113	*	*	*	*	*
Kaimite								
Sylvite								
Russia, carbonate of potash	{ 2,344°	*	{ 62,823	6,282	146,692	14,669	137,858	14,062
Spain:	*		{ 115,980	31,315	194,964	90,942	220,770	46,673
Crude salts			3,947	*	*	*	*	*
Potassic earth	†		27,734	4,021	243,233	24,323	243,994	*
United States, crude salts	†		1,000	29	850	*	850	*
	†		40,779	23,086	94,464	54,349	97,812	55,873

* Data not available.

° Under Austrian control in 1913.

† Included under Germany.

‡ Figures not available, production unimportant.

§ Exports.

¶ Figures relate to merchantable products

last factor is important because platinum compounds are frequently used. If possible, the analyst should use methods that have been adopted as official. They have been studied carefully by many workers and they are designed primarily to assure accuracy. If speed is important the volumetric or centrifugal methods should be considered. In cases where interfering substances are known to be absent, it is often possible to adopt special short methods that give sufficient accuracy.

Methods of determining potassium are fixed primarily by two characteristics of this element. The first of these is the extreme solubility of nearly all potassium compounds in water. This frequently makes it necessary to remove by precipitation many other elements commonly present before the potassium determination can be carried out and to use a special solvent, such as ethyl alcohol, in order to obtain proper solubility relationships. The second characteristic of importance is the great similarity of potassium compounds to those of the other alkali metals and to ammonium compounds. The latter give the most trouble and in nearly all potassium determinations the preliminary elimination of all ammonium compounds is essential.

The methods of determining potassium are discussed under two major headings, qualitative and quantitative. Qualitative methods are considered only briefly because in analyzing fertilizer materials the absence or presence of potassium is usually known in advance. Three methods only, the flame test, the cobaltinitrite method, and the sodium bismuth thiosulfate method are discussed. Quantitative methods are considered in three groups, gravimetric, volumetric and miscellaneous methods. The gravimetric and volumetric groups overlap somewhat owing to the fact that some of the methods may be used for both gravimetric and volumetric determinations by making slight changes in the procedure. Under miscellaneous methods are discussed those not readily classified as either volumetric or gravimetric; the polarimetric method of Wrobel is an example of such a method.

QUALITATIVE DETECTION OF POTASSIUM

Flame Test.—A convenient and effective qualitative test for potassium is made by dipping a platinum wire loop into a strongly acid solution of the supposed potassium compound and viewing through a piece of cobalt glass the coloration produced when it is held in the non-luminous flame of a Bunsen burner. The red-purple tint produced is compared with that

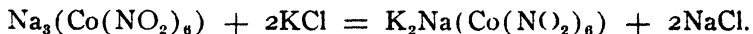
coming from a pure potash salt similarly treated. If a fertilizer sample gives no indication of potash when so treated it may be safely concluded that it does not contain any weighable quantity.

A modification of the flame test has been proposed by Rogers¹ whereby the approximate quantitative estimation of potassium can be made. A platinum loop dipped in an aqueous solution of a potash salt of definite concentration is subjected to a flame test along with a similar test of a solution of a pure salt, the persistence of the flame test being used as an approximate estimate of the potash content.

Flame Spectrum.—The flame coloration may be examined with the spectroscope. At low temperatures potassium gives a double red line at 769.9 and 765.5 $\mu\mu$ and a faint violet line at 404.4 $\mu\mu$. At higher temperatures lines appear in the yellow at 583.2, 580.2 and 578.2 $\mu\mu$ and in the green at 535.1 and 511.3 $\mu\mu$.²

Sodium Cobaltinitrite Method.—Possibly one of the most delicate processes for the qualitative detection of potassium is that of de Koninck,³ which was developed a number of years later as a quantitative procedure for determination of potash under the name of the cobaltinitrite process. As described by de Koninck, a 10 per cent sodium nitrate solution is mixed with some cobalt chloride and acetic acid and upon addition to potassium chloride gives a distinct yellow precipitate with even a dilution of 1 to 1000. Salts of magnesia, calcium, barium, strontium, iron, alumina and zinc are not precipitated.

Sodium cobaltinitrite, $\text{Na}_3(\text{Co}(\text{NO}_2)_6)$, precipitates yellow potassium sodium cobaltinitrite from neutral or slightly acid solution.



Ammonium salts give a similar precipitate, but moderate amounts of alkaline-earth elements or of lithium and sodium do not interfere. The solution must not be alkaline or $\text{Co}(\text{OH})_3$ will be precipitated.

The sodium cobaltinitrite reagent, prepared as follows, permits the detection of 0.3 mg. of potassium within 10 minutes. Dissolve 230 grams of sodium nitrite in 500 cc. of water and add 155 cc. of 6 normal acetic acid and 30 grams of cobaltous nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Let the mixture stand overnight, filter, and dilute to 1 liter.

¹ *Chem. Met. Eng.*, **25**, 161 (1921); *C. A.*, **15**, 3044.

² Treadwell and Hall, *Analytical Chemistry*, 4th ed., Vol. 1. Qualitative, p. 82.

³ *Z anal. Chem.*, **20**, 390 (1881); Curtman, *Ber.*, **14**, 1951 (1881).

If the reagent is prepared according to the following directions of Biilmann,¹ as little as 0.0009 mg. of potassium can be detected in the presence of 4000 equivalents of sodium. Dissolve 150 grams of sodium nitrite in 150 cc. of hot water and allow the solution to cool to about 40°, which will cause the deposition of some sodium nitrite crystals. Add 50 grams of cobalt nitrite crystals, stir rapidly, and add 50 cc. of 50 per cent acetic acid in small portions; stopper the flask and shake vigorously. Pass a rapid stream of air through the liquid and then allow to stand quietly overnight. In the morning more or less brown precipitate will be found on the bottom of the flask due to a little potassium salt present in the sodium nitrite. Siphon off the clear liquid through a filter and add to the filtrate, while stirring, about 200 cc. of alcohol in small portions; this causes the precipitation of the greater part of the dissolved sodium cobalt-nitrite.

After several hours, filter off the precipitate and drain it as completely as possible with the aid of suction. Wash the precipitate four times with 25 cc. portions of alcohol and twice with ether. Recrystallize the salt by dissolving 10 grams of solid in 15 cc. of water and precipitating with 35 cc. of alcohol. The dry salt keeps very well, but the aqueous solution decomposes gradually. To obtain the best results, the reagent should be prepared freshly by dissolving 1 gram of the salt in 10 cc. of water.

Sodium Bismuth Thiosulfate Method.²—The little known and very sensitive Pauly-Carnot reagent, sodium bismuth thiosulfate, gives in potassium salt solutions a crystalline yellow precipitate. This reagent has the advantage that ammonium salts give no reaction, while strontium and barium give white precipitates.

According to P. Löhr³ the test is conducted as follows:

Prepare two solutions, the first by dissolving 24.8 grams of sodium thiosulfate in 50 cc. of distilled water, and the second by dissolving 9.73 grams of basic bismuth nitrate in the least possible amount of hydrochloric acid and then making up to 50 cc. with very dilute hydrochloric acid. Dissolve 1 gram of the salt to be tested in a test tube with distilled water, place 1 cc. of this solution in another test tube, and dilute with water. To 1 cc. of this second solution add 5 drops of thiosulfate solution and then 5 drops of bismuth chloride. (Do not make these additions in the reverse order.) Dilute this mixture with 2 cc. of distilled water. (This should result in a clear, bright yellow solution.) Add quickly with shaking 20 cc. of absolute alcohol; if the smallest amount of potassium is present, a yellow crystalline precipitate will form. The color is that of yellow potassium chromate.

¹ *Z. anal. Chem.*, **39**, 284 (1900). The translation is that given in Treadwell-Hall.

² L. Tietjens, *Laboratoriumsbuch für die Kaliindustrie*, 1924, p. 22.

³ *Z. öffentl. Chem.*, **10**, 421, 439 (1904).

It should be noted that this precipitate appears very quickly; yellow and white turbidities appearing later are to be ignored. It is characteristic that the potassium salt comes down as a clear yellow and crystalline precipitate only when it is present in excess.

(For other methods the reader is referred to the standard works on qualitative analysis.)

QUANTITATIVE METHODS

Preparation of Solution.—In accordance with the fertilizer control regulations of the several states of the union and of the regulations in use in the various countries exercising fertilizer control, only the potash soluble in water is taken into account in reporting the results of fertilizer analysis.

In a number of countries, including the United States, the potash is brought into solution by boiling the sample with hot water, or it is washed with a number of successive portions of boiling water, as is the procedure in the methods of the Association of Official Agricultural Chemists; in a number of other countries solution is effected by means of cold water. In any event, the cooled solution is made up to the mark, and the contents are well mixed before proceeding.

In the case of the Lindo-Gladding process, an excess of ammonium hydroxide and ammonium oxalate solution is added to the hot solution, and the liquid is cooled before diluting the volume to the calibration mark.

Destruction of Organic Matter.—*Direct Ignition.*—The simplest and most direct method for destroying organic matter is by direct ignition. The incineration may be conducted in the open air or in a muffle, the temperature being kept as low as possible; in no case should a low red heat be exceeded. Burning in a muffle is preferred because only a moderate draft is produced and a more even heat can be maintained. If a diffused flame is used to avoid local overheating excellent results can be obtained in an open dish or one partly closed with a lid. In using a muffle the heat should be only great enough to secure combustion and the even and uniform temperature that may be maintained by the use of the electric muffle furnace strongly commends the use of this source of heat.

Ignition with Sulfuric Acid.—Sulfuric acid may be used to secure better incineration. By this procedure the bases, which by direct ignition are usually secured as carbonates, are obtained as sulfates. The method adopted by the Association of Official Agricultural Chemists specifies that

the sample be saturated with sulfuric acid and ignited in a muffle until all organic matter is destroyed. If the ash is moistened when cool with a little hydrochloric acid and warmed, it is more easily detached from the dish. The solution is completed with the addition of water and the required reagents before the volume is finally made up to the mark. This method has several advantages over the direct ignition method. For example, if potassium chloride is present in the ash, the danger of loss of potash from volatilization is lessened by the sulfate process. Moreover, in this method there is not so much danger of occluding particles of carbon in the ash as there is in the direct ignition method.

Blumenthal, Peter, Healy and Gott¹ have made a study of the most favorable conditions for ashing organic materials and make the following statements :

- (1) The most common source of loss is by spattering and volatilization in removing organic matter and ammonia salts.
- (2) Burning off carbon in a muffle furnace leads to more uniform results than direct heating over a free flame.
- (3) Converting the potassium salt to sulfate reduces volatilization losses.
- (4) Moistening the sample with sulfuric acid is not sufficient; enough sulfuric acid should be added to act as an oxidizer for carbon and to convert all inorganic compounds present to sulfates.
- (5) Direct evaporation of the sample with nitric and sulfuric acids, preliminary to burning off organic matter, has proved the best method of securing uniform results and has materially reduced volatilization losses.

Moist Combustion.—Errors arising from the volatilization of potassium salts or mechanically from spattering when igniting to destroy ammonium salts and organic matter may be quite large. These errors are avoided in the de Roode² method and in the modifications of Moore,³ Veitch⁴ and Keitt and Shiver⁵ by digesting with aqua regia instead of igniting. Keitt and Shiver claim that large amounts of ammonium salts and organic matter can be eliminated by their procedure (p. 383) and that the method is satisfactory for fertilizer materials in general. They recommend evaporating twice with aqua regia.

¹ *J. Ind. Eng. Chem.*, **9**, 753 (1917).

² *J. Am. Chem. Soc.*, **17**, 86 (1895).

³ *Ibid.*, **20**, 342 (1898).

⁴ *Ibid.*, **27**, 56 (1905).

⁵ *J. Ind. Eng. Chem.*, **10**, 215 (1918); **11**, 1049 (1919).

GRAVIMETRIC METHODS

CHLOROPLATINATE METHODS

*Involving the Direct Weighing of Potassium Chloroplatinate.*¹—The method of Lindo² consists in obtaining a solution containing only the chlorides of sodium and potassium, converting the chlorides into chloroplatinates by evaporating nearly to dryness with sufficient chloroplatinic acid and adding strong alcohol. Sodium chloroplatinate dissolves and is separated from the potassium chloroplatinate by filtration. The potassium salt is washed with alcohol, dried, and weighed. This method with some changes forms the present alternative method of the A.O.A.C. and is official in several foreign countries. The detailed procedure is given in *Methods of Analysis, A.O.A.C.*

In this method it is necessary that all sulfate be carefully removed because of the slight solubility of sodium sulfate in alcohol. Even when sufficient chloroplatinic acid is used to combine with both the sodium and the potassium, the less soluble sodium sulfate is still precipitated and contaminates the potassium chloroplatinate precipitate. It is difficult to secure a potassium chloroplatinate precipitate that is all K_2PtCl_6 . It may contain some compounds such as H_2PtCl_5OH or H_2PtCl_5O , and probably also a little sodium chloride. Errors arising from such contamination have been partially compensated in some modifications of the method by the use of 80 per cent alcohol instead of the very strong alcohol. Potassium chloroplatinate is more soluble in the weaker alcohol and this negative error compensates the positive error, due to contamination of the precipitate, quite satisfactorily in many cases. Some authorities prefer to wash with 96 per cent alcohol and calculate the results, using a factor determined experimentally by the analysis of known mixtures. This is satisfactory if the conditions of the analysis are similar to those under which the factor was determined.

Volatile acids, organic compounds, ammonium salts, etc., are most easily eliminated by ignition, but potassium chloride, if present, will also be volatilized unless the ignition is carefully done below a red heat. Potassium

¹ The compound H_2PtCl_6 is often called platinum chloride, but the term chloroplatinic acid is preferred since platinum chloride is really $PtCl_4$. The latter compound precipitates potassium only after long standing, if at all. Treadwell and Hall (*Analytical Chemistry*), Hillebrand and Lundell, (*Applied Inorganic Analysis*, 1929), Mellor (*Quantitative Inorganic Analysis*) and others prefer the term chloroplatinic acid and the corresponding term for the potassium salt, potassium chloroplatinate. These terms are used in this chapter except in direct quotations that contain the other forms.

² *Chem. News*, 44, 77, 86, 97 and 129 (1881).

sulfate, however, is not easily volatilized and it would be advantageous to convert the potassium to the sulfate if the error due to sodium sulfate, mentioned above, did not prevent such a procedure. Gladding¹ avoided this difficulty by washing the sodium sulfate out of the precipitate, after the removal of the excess chloroplatinic acid, by a water solution of ammonium chloride in which the sodium sulfate is quite soluble. To avoid loss of potassium chloroplatinate the wash liquid is previously saturated with the pure salt. It is important when using this procedure that the ammonium chloride wash be saturated with the potassium salt at the temperature at which the analysis is carried out, since otherwise some potassium chloroplatinate may be added to the precipitate or some of the precipitate may be dissolved. The Gladding modification of Lindo's process, with some refinements introduced later, is the official method of the A.O.A.C. It was first adopted as official in 1887.

In the de Roode method, as already stated, ignition to destroy organic matter is entirely avoided. Moore's² modification of this method was tested by Veitch² on a wide variety of fertilizer materials with good results.

Keitt and Shiver² claim good results with a modified de Roode method in the presence of "any amount of ammonium salts, organic matter, nitrate of soda or phosphatic material that will be used in a manipulated fertilizer, or that may be present in natural fertilizing materials." The procedure of this method, which is similar to that of Moore's, is as follows.

Place 10 grams of the material to be analyzed in a 500 cc. flask, add 300 cc. of water, boil 30 minutes, cool, make up to the mark, mix thoroughly, and filter through a dry filter paper, discarding the first few cubic centimeters of filtrate. Place a 50 cc. aliquot of the filtrate in a thin porcelain dish and add 30 cc. of aqua regia after putting the dish on a hot plate. Evaporate to dryness, add 30 cc. of aqua regia, and again evaporate to dryness; take up the residue with a little hot water, add 10 cc. of concentrated hydrochloric acid, and again evaporate to dryness. Take up the residue with hot water and add chloroplatinic acid solution. Evaporate almost to dryness, remove from the water bath, and by gentle swirling cover the dried portion with the part still liquid and evaporate a little more. Cover the precipitate with acidulated alcohol (prepared by adding 75 cc. of concentrated hydrochloric acid to 1000 cc. of 95 per cent alcohol and then passing in dry hydrochloric acid gas until 1 cc. of the alcohol neutralizes 2.25 cc. of normal alkali, using phenolphthalein as an indicator) and allow to stand for an hour, thoroughly breaking up the precipitate with a policeman. Wash the precipitate with acidulated alcohol until the washings are colorless, pouring the washings through a tared filter paper. Trans-

¹ U. S. Dept. Agr. Chem. Bull., 7, p. 38 (1885).

² *Loc. cit.*

fer the precipitate to the filter, wash at least seven times with ammonium chloride wash (prepared by adding 200 grams of ammonium chloride to 1000 cc. of water and saturating in the cold with potassium chloroplatinate) and five times with 80 per cent alcohol, dry, and weigh.

This procedure requires no platinum dishes and eliminates the precipitations required in the Lindo-Gladding process.

Involving the reduction of the precipitated potassium chloroplatinate.—When analyzing complex materials it is frequently better to reduce the potassium chloroplatinate and weigh the metallic platinum. The preliminary purification of the solution to be analyzed is much simpler when the chloroplatinate is to be reduced and usually it is only necessary to remove ammonia and organic matter. Platinum is an ideal precipitate because it can be ignited or treated with strong acids (except aqua regia) without danger of loss or decomposition. The weight of the platinum, however, is less than one-half that of the chloroplatinate, and losses during washing or otherwise are therefore more important. Many methods in which metallic platinum is weighed have been suggested.

The process of Corenwinder and Contamine,¹ specifying sodium formate as the reducing agent, has been used to a considerable extent in Europe. It is given in full among the Spanish official methods.

Neubauer's² modification of Finkener's process (for details see German official methods, p. 428) is used rather widely. The reduction is accomplished with hydrogen or illuminating gas.

A simple reduction method is that recommended by Hilgard.³ The potassium chloroplatinate is reduced in a crucible, the lower half of whose interior is covered with a film of platinum sponge formed by the previous ignition of about a decigram of potassium chloroplatinate. In the presence of this sponge the decomposition is effected readily even at a comparatively low heat. About two drops of hydrochloric acid are added to the crucible when cool, and if after gentle warming a yellow color appears, a little oxalic acid is added and the ignition is continued. By washing with acidified water, soluble substances are removed.

A novel departure from the more common reduction processes is proposed by Bornträger,⁴ whereby the reduction of the solution of platinum double salt is effected by a potash soap solution. The mixture of double salt and platinum oleate is ignited in a porcelain crucible and washed with hot water.

¹ Bull. Soc. Ind. du Nord, 1879.

² Z. anal. Chem., 39, 481 (1900).

³ Ibid., 32, 184 (1893); J. Chem. Soc., 64, pt. 2, 300 (1893).

⁴ Ibid., 188 (1893).

Jean and Trillat¹ propose that the purified double salt be dissolved in water, made alkaline with sodium hydroxide, warmed and reduced with formaldehyde.

Villiers and Borg² propose washing the potassium chloroplatinate with a mixture of alcohol and ether, dissolving the precipitate in hot water, adding a little pure hydrochloric acid, and reducing with finely divided magnesium, which is added gradually. After washing, the reduced platinum is ignited and weighed.

Sonstadt³ proposes the reduction of the potassium chloroplatinate by means of metallic mercury; a small excess of the latter is placed in a small porcelain crucible and the chloroplatinate is then added. Heat is applied gently for some time and then the temperature is raised high enough to drive off the excess of mercury. The author states that the reaction is very delicate—1 part in 3,000,000.

Among the chemists who suggest the reduction of the aqueous solution of the double salt by means of metallic magnesium are the following: Atterberg, *Z. anal. Chem.*, **51**, 483 (1912); Fiechter, *Z. anal. Chem.*, **50**, 629 (1911); Crete, *Chem. Ztg.*, **34**, 1040 (1910); de Koninck, *Z. anal. Chem.*, **21**, 406 (1882); Ledoux, *Bull. soc. chim. Belg.*, **28**, 51 (1914).

Hicks,⁴ who studied the reduction method, comments as follows:

The method is applicable in the presence of chlorides, sulfates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and aluminum, and is especially suited for the estimation of potassium in potassium salts, salines and mixed fertilizers in which only the quantity of potassium is desired, and also in organic fertilizers after an appropriate modification to remove ammonia and other organic bases which interfere with the determination.

The method used by Hicks follows:

Prepare the solution in the usual way, acidify slightly with hydrochloric acid, add chloroplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present, and evaporate the solution on the steam bath to a sirupy consistency, *i. e.*, until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80 per cent strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. (The alcoholic solution should be colored if an excess of chloroplatinic acid has been used.) Pour the liquid through a small

¹ *Bull. soc. chim.*, **7** (3), 228 (1892), *J. Chem. Soc.*, **64**, 46 (1893).

² *Compt. rend.*, **116**, 1524 (1893).

³ *J. Chem. Soc., Trans.*, **67**, 984 (1895).

⁴ *J. Ind. Eng. Chem.*, **5**, 650 (1913).

filter, using suction, and before adding more alcohol rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. (Three or four washings usually suffice.) Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 1 cc. of concentrated hydrochloric acid and approximately 0.5 gram of magnesium ribbon (which has been previously washed in water) for every 0.2 gram¹ of potassium present, stirring the solution and holding the magnesium at the bottom of the beaker by means of a glass rod. When the magnesium has practically dissolved, add a few cubic centimeters of dilute hydrochloric acid and allow the flocculent platinum to settle. The supernatant liquid should be perfectly clear and limpid like water if reduction is complete. To make sure add more magnesium, in which case the solution will darken if reduction be incomplete. Now add concentrated hydrochloric acid and boil to dissolve any basic salts, filter, wash thoroughly with hot water, ignite, and weigh. From the weight of platinum thus obtained calculate the percentage of potassium.

Horsch² commends the following reduction process:

The chloroplatinate is dissolved in boiling water and transferred to a platinum crucible, where it is reduced by alcohol on the boiling water bath; more alcohol is added and the heating is repeated.

Schumm³ proposes the electrolytic reduction of the water solution of the double salt, the platinum being deposited upon the interior of a platinum crucible.

Finkener,⁴ in 1886, was probably the first to use a reduction method. He did not weigh metallic platinum but reduced the potassium chloroplatinate by igniting in hydrogen, extracted the residue with water, and weighed the potassium chloride.

Sources of Error.—In most gravimetric procedures the precipitate to be weighed is thrown down from a comparatively large amount of solution which retains the other dissolved substances. All the important methods of determining potassium, however, are extraction methods, that is the potassium precipitate is obtained by evaporating with the precipitating agent. The resulting mass of salts, which consists of everything that was in the solution, is then extracted with wash liquids to dissolve everything but the potassium salt. Impurities which cannot be satisfactorily removed by extraction must be separated by precipitation previous to precipitating the potassium. This provides opportunity for adsorption or

¹ Frechter, *Z. anal. Chem.*, **50**, 632 (1911).

² *Compt. rend.*, **183**, 167 (1919); *J. Chem. Soc.*, **116**, pt. 2, 118 (1919).

³ *Z. anal. Chem.*, **40**, 385 (1901).

⁴ *Pogg. ann.*, **9**, 637 (1866).

occlusion of the potassium by these precipitates. Keitt and Shiver¹ made a study of the occlusion of potash by the precipitates formed on the addition of ammonia and ammonium oxalate in the Lindo-Gladding method. They found that it was impossible to wash the occluded potash out of the precipitate with hot water but that it could be recovered to a certain extent by repeatedly dissolving the precipitate in hydrochloric acid, diluting to a large volume, precipitating with ammonia and ammonium oxalate, filtering, and determining potash in the filtrates and washings. Errors due to occlusion by precipitates are not serious under average conditions.

Water-soluble potash in fertilizers was formerly determined by boiling the sample for some time with water and then allowing the solution to stand before finally making the solution up to the mark. It was contended that occlusion under these conditions took place to a marked extent and that potash could not be completely dissolved out of the fertilizer. Experiments having shown that a smaller sample, subjected to frequent washings on the filter with boiling water, would give up its potash more readily, the official method of the A. O. A. C. was so modified in 1912 as to provide for the latter method of effecting the solution.

Winton observed a distinct difference in the crystals of potassium chloroplatinate when obtained from concentrated and dilute solution.² When chloroplatinic acid is added to a concentrated solution of potassium chloride, a large part of the salt which is formed is precipitated in a pulverulent state, the remainder being deposited on evaporation. After being treated with alcohol, filtered, and dried, the double salt is found in the state of a fine powder which, when examined under the microscope, is found to consist largely of radiating crystals. The characteristic form is one having six arms formed by the intersection, at right angles, of three bars. Numerous globular cavities in the crystals are observed in which mother liquid is enclosed. For this reason the salt is not easily dried at 100° C., and when so dried loses additional moisture at 130°, and still more at 160°. The total additional loss from this cause, after drying at 100° may amount to as much as 0.6 per cent of potassium chloride. When, however, the solution of the potassium salt is so dilute that no precipitate at all is formed on the addition of chloroplatinic acid, the double salt is formed slowly during the evaporation. It occurs exclusively as octahedra. These octahedra are comparatively free of cavities, and they give up practically all their moisture when dried at 100°.

¹ *J. Ind. Eng. Chem.*, **10**, 994 (1918).

² *J. Am. Chem. Soc.*, **17**, 453 (1895).

In several procedures the solution is made up to volume without removing the precipitates formed in the preliminary treatment of the solution. If the amount of such precipitates is large, an appreciable error is caused by their volume.

In the manufacture of mixed fertilizers it sometimes happens that the analysis of the completed product does not show as much water-soluble potash as should be expected. This is most likely to occur after prolonged storage of the mixed fertilizer and is probably due to the slow formation of insoluble potassium compounds. Super phosphate usually contains 1-2 per cent of fluorine in the form of hydrofluosilicic acid and reactive fluosilicates. It has been suggested that the decrease in water-soluble potash noted when mixtures containing potash and superphosphate are stored may be due to the formation of potassium fluosilicate, which is comparatively insoluble.¹

Recovery of Platinum from Residues and Scraps and the Preparation of Chloroplatinic Acid.—Platinum is the most expensive reagent ordinarily used in fertilizer laboratories. The amount required in each analysis varies, but it may be as much as 0.3 gram; it is important, therefore, to collect all platinum residues and scraps and work them up periodically to prepare metallic platinum or platinum solutions.

(1) *Preparation of Chloroplatinic Acid from Metallic Platinum.*—Iridium is usually contained in commercial metallic platinum. Although normally insoluble in aqua regia it is soluble to some extent in that reagent when alloyed with platinum. When platinum dissolves in aqua regia to form chloroplatinic acid some chloroplatinous acid (H_2PtCl_4) and some nitroso platinic chloride ($\text{PtCl}_6(\text{NO})_2$) are formed at the same time. Both these impurities and the iridium must be carefully eliminated because their presence causes inaccurate results in the potash determination. Proceed as follows:

Clean all pieces of metallic platinum by boiling with concentrated hydrochloric acid and washing with water. Place the cleaned platinum in a large flask, cover it with concentrated hydrochloric acid, and add successive small portions of nitric acid while heating gently on a water bath. All the platinum is dissolved but part of the iridium remains undissolved as a black powder. Decant the solution into a large evaporating dish and evaporate to a sirupy consistency. Take up the residue with water, add sodium formate and sodium carbonate gradually until the solution is alkaline, and heat to boiling. Care should be taken that the evaporating dish is only partially filled with solution in order to avoid loss of platinum by the sudden and violent evolution of carbon dioxide that frequently occurs. (The platinum and

¹ Private communication from K. D. Jacob, U. S. Bur. Chem. and Soils.

iridium are deposited as black powders.) Decant the supernatant liquid, and wash the residue several times with dilute hydrochloric acid to remove the sodium salts and then with water to remove the acid. Dry the residue and ignite strongly in a porcelain crucible over a blast lamp (this renders the iridium insoluble in aqua regia) and weigh. Dissolve as before in hydrochloric and nitric acids at the lowest possible temperature. Evaporate with water to convert any nitroso platinic chloride formed into chloroplatinic acid: $\text{PtCl}_6(\text{NO})_2 + \text{H}_2\text{O} = \text{NO} \uparrow + \text{NO}_2 \uparrow + \text{H}_2\text{PtCl}_6$. (Some nitric and nitrous acids are formed from the oxides of nitrogen and these cause the re-formation of some nitroso platinic chloride.) Evaporate alternately with hydrochloric acid and with water until no more nitrous fumes are evolved, thus completely eliminating the nitroso compound.

Dittmar and McArthur¹ doubt if it is possible to destroy all the nitroso platinic chloride by this procedure. They recommend dissolving the metal with hydrochloric acid and chlorine. Noyes and Weber² emphasize the importance of removing nitric acid from the platinum solution. The solution resulting from the evaporation with water and with hydrochloric acid is brown and contains some chloroplatinous acid which must be oxidized to chloroplatinic acid as follows:

Saturate the warm solution with chlorine gas, causing it to become much lighter colored, and evaporate to a sirupy consistency. Cool, dissolve the resulting yellowish brown crystalline mass in a little cold water and filter off the insoluble iridium. Ignite the iridium in a porcelain dish, cool, weigh, and deduct from the previous weight of the mixture to obtain the weight of the platinum. Dilute the filtrate with water until 100 cc. of solution contains 10 grams of platinum.

Tietjens³ and Metge⁴ recommend that the precipitated platinum be boiled with concentrated nitric acid, in addition to the hydrochloric acid washings, before being dissolved in aqua regia. The evaporation of the platinum solutions is continued until a drop removed on a glass rod solidifies. Platinous compounds may be converted to the platinic state by heating with fuming hydrochloric acid and a little nitric acid. Both platinous and nitroso compounds may be destroyed more quickly by the addition of pure hydrogen peroxide solution prior to the final dilution to the desired strength. Iridium may be removed by addition of ammonium chloride to the solution containing platinum and iridium. Insoluble ammonium chloroplatinate precipitates, leaving the iridium in solution. The precipitate will be contaminated with iridium if the iridium is present in the

¹ *Trans. Roy. Soc. Edin.*, **33**, ii., 561 (1887).

² *J. Am. Chem. Soc.*, **30**, 13 (1908).

³ *Laboratoriumsbuch für die Kaliindustrie*, 2nd ed., 1924.

⁴ *Laboratoriumsbuch für Agriculturchemiker*, 2nd ed., 1926.

quadrivalent state. Even in the trivalent state the separation is not clean cut and should be repeated several times.¹

Hillebrand and Lundell² state that the best method of dissolving platinum black is the electrolytic procedure of Weber.³ This method requires the following special apparatus. (Fig. 2).

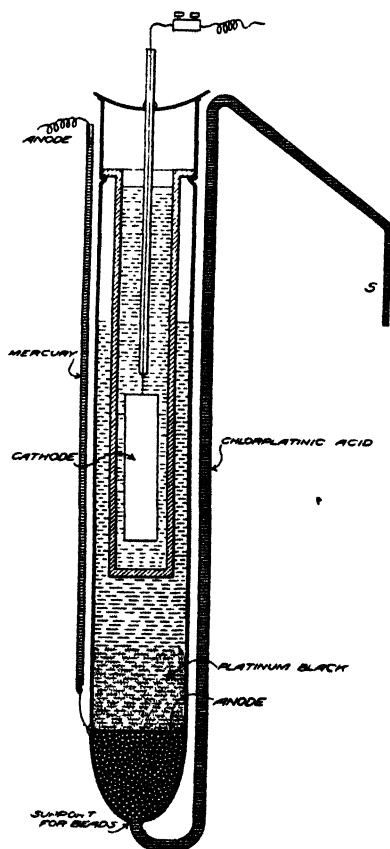


Fig. 2.—Apparatus for Making Pure Chloroplatinic Acid.

A cylindrical tube about 4 cm. in diameter and 35 cm. long, ends in a narrow glass tube of about 4 mm. bore, which is given the form of a siphon. An anode of thin sheet platinum, perforated with numerous small pinholes, just fits into the tube and rests firmly on the glass beads which fill the bottom of the large tube.

¹ Private communication from R. Gilchrist, U. S. Bur. Standards.

² Applied Inorganic Analysis, 1929, p. 39.

³ *J. Am. Chem. Soc.*, **30**, 29 (1908).

A platinum wire is welded to the anode, sealed through the side wall of the large tube and then into the end of a narrow tube that is filled with mercury to make the anode connection for the current. A cathode chamber consisting of a porous porcelain filter about 18 cm. long and 25 mm. in diameter is suspended from three notches pressed into the wall of the large tube. The cathode consists of a sheet of platinum 4-5 cm. long and 2-3 cm. wide, to which is welded a platinum wire. The wire is sealed into the end of a glass tube and serves as the cathode connection for the current. The whole cathode assembly is supported in the cathode chamber by a perforated watch-glass through which the tube carrying the platinum wire passes. The watch-glass also serves as a cover for the apparatus.

The platinum is placed on the anode plate and here washed with hydrochloric acid until clean, the wash-waters being drawn off through the siphon-shaped tube. The large tube is then filled with concentrated hydrochloric acid until, with the cathode chamber inserted, the acid stands more than half way to the top of the cathode chamber. The porous cylinder is then inserted, filled to the top with hydrochloric acid and the cathode inserted. A current of 8-10 amperes may be passed from 110-120 volt direct current source, a lamp bank or a rheostat being used for control. If the cell heats, it may be cooled by placing in water. With the proper adjustment of the height of hydrochloric acid in the anode cell, the heavy layer of chloroplatinic acid is delivered at *S*, drop by drop. If towards the end of the operation, when the platinum is nearly all dissolved, small bubbles of chlorine appear, fresh acid should be brought into the neighborhood of the platinum black or the current should be decreased. The action of the cell is quite rapid. Using a current of 8 amperes, Weber dissolved 64 grams of platinum in $4\frac{1}{2}$ hours.

In concentrating the solution of chloroplatinic acid after it is prepared, chlorine is passed through it for a time to remove any platinous compounds that may have been formed during the electrolysis. This procedure yields a solution free from nitrosoplatinic acid, platinous acid and hydroxychloroplatinate, all of which are objectionable.

(2) *Preparation of Chloroplatinic Acid from Platinum Residues.*—Platinum residues in fertilizer laboratories consist of potassium chloroplatinate precipitates and alcoholic wash-waters. When the latter are allowed to stand platinum black precipitates slowly and acetone is formed, which renders the alcohol unfit for further use and difficult to purify. The following procedure described by Hough¹ permits the recovery of both the alcohol and the platinum.

Add ammonium chloride crystals to the alcoholic filtrate immediately after the analysis, using 1 gram of crystals for each 300 cc. Mix well, allow to stand until clear, and filter. Allow the filtrate to accumulate until sufficient is obtained for rectification and then distil off about three-fourths of the liquid. (The distillate will be 83-85 per cent alcohol, which is suitable for re-use in the Lindo-Gladding method.) Add the potassium chloroplatinate residues to the ammonium chloroplatinate obtained above, dissolve in hot water, add a few cubic centimeters of hydrochloric

¹ *Ind. Eng. Chem. Anal.*, ed., **1**, 162 (1929).

acid (1 + 2), heat to boiling, and reduce by adding magnesium powder gradually until a small excess is present. When the precipitation of the platinum is complete, add slowly sufficient concentrated hydrochloric acid to dissolve the excess magnesium, boil several minutes, filter off the platinum, and wash well. Prepare the chloroplatinic acid solution as described under "Preparation of chloroplatinic acid from metallic platinum." Iridium is not present if it was properly eliminated when the original solution was made up from metallic platinum.

According to Treadwell and Hall,¹ when an alcoholic solution of chloroplatinic acid is evaporated, chloroplatinous acid and ethylene are formed. These react to form ethylene platinous chloride, which does not precipitate either ammonium or potassium. When the solution of this compound is evaporated it is changed into an insoluble substance that is explosive when dry and only decomposed by strong ignition.

Metge² recovers the platinum in the residues and washings as follows:

Dilute the alcoholic washings with about one-third their volume of water, add sodium carbonate or bicarbonate and the chloroplatinate residues, and heat on a water bath until the liquid above the platinum black is clear and only slightly yellow. (Any barium sulfate present in the chloroplatinate residues will be converted to carbonate by this procedure. Unless the barium carbonate and sodium sulfate are completely washed out, barium sulfate will be re-formed later when acid is added and a small amount will remain dissolved in the chloroplatinic acid solution.) Boil the reduced platinum with water to dissolve the sodium sulfate and barium carbonate, decant, and wash several times by decantation with hydrochloric acid and water; ignite to destroy organic matter, boil once with concentrated nitric acid, decant, and prepare chloroplatinic acid as described above under "Preparation of chloroplatinic acid from metallic platinum."

Tietjens³ reduces alternately with zinc. Treadwell and Hall and Mellor⁴ distil the alcohol from the washings, take up the residue with water, add the potassium chloroplatinate residues, and reduce at boiling temperature after adding a solution consisting of 21 grams of sodium hydroxide and 8-10 cc. of glycerine in 100 cc. of water.

A good test of the platinum solution is described by Tietjens³ and by Metge² as follows:

Dissolve 7.640 grams of pure potassium chloride and about 1.2 grams of pure sodium chloride in distilled water and make up to 500 cc. Determine the potassium

¹ Analytical Chemistry, Vol. I, 5th ed., p. 286.

² *Loc. cit.*

³ *Loc. cit.*

⁴ Quantitative Inorganic Analysis, 1913.

in this solution. If the theoretical value is obtained, the solution may be assumed to be satisfactory. The addition of sodium chloride is necessary since small quantities of sulfates present in the platinum solution might otherwise be overlooked and later cause high results.

TABLE XX.*—DENSITY AND PERCENTAGE OF PLATINUM IN AQUEOUS CHLOROPLATINIC ACID SOLUTION AT 15°.

Density	Platinum	Density	Platinum	Density	Platinum
	Per cent		Per cent		Per cent
1.000	0.579	1.118	10.42	1.450	20.26
1.018	1.158	1.201	11.00	1.469	20.84
1.027	1.737	1.214	11.58	1.488	21.42
1.036	2.327	1.227	12.16	1.500	21.99
1.046	2.895	1.242	12.73	1.523	22.57
1.056	3.474	1.256	13.31	1.546	23.15
1.066	4.052	1.270	13.90	1.568	23.73
1.076	4.630	1.285	14.47	1.591	24.31
1.086	5.209	1.300	15.05	1.615	24.80
1.097	5.788	1.315	15.63	1.641	25.48
1.108	6.367	1.330	16.21	1.666	26.05
1.119	6.946	1.346	16.79	1.688	26.63
1.130	7.525	1.362	17.36	1.712	27.20
1.141	8.115	1.387	17.94	1.736	27.78
1.153	8.683	1.395	18.52	1.760	28.36
1.165	9.262	1.413	19.10	1.785	28.94
1.176	9.840	1.431	19.60		

* Tietjens, *Laboratoriumshuch für die Kalundustrie*

Alcohol.—In the two important methods of determining potassium, the chloroplatinate and perchlorate methods, an ethyl alcohol wash is used to free the potassium precipitates from other chloroplatinates or perchlorates and from other compounds soluble in alcohol. For the chloroplatinate method some authorities use 80 per cent alcohol while others specify 96 per cent (see p. 383). According to Precht¹ one part of potassium chloroplatinate dissolves in 37,300 parts of 96 per cent alcohol, or in 26,400 parts of 80 per cent alcohol. Since the solubility of potassium perchlorate increases rapidly with increasing dilution, the wash alcohol for the perchlorate method must always be 96 per cent or stronger. Table XXI shows the amount of potassium perchlorate dissolved in 100 cc. of alcohol of various strengths.

In both methods the alcohol is often previously saturated with the potassium salt to be washed in order to reduce the losses due to the solvent action of the alcohol. Other reagents may be added for this purpose or to improve the washing action of the alcohol.

¹ *Z. anal. Chem.*, **18**, 513 (1879); compare *Landw. Vers. Sta.*, **47**, 104 (1896).

TABLE XXI.¹—SOLUBILITY OF POTASSIUM PERCHLORATE IN ALCOHOL OF DIFFERENT STRENGTHS.

Alcohol concentration Percentage, by weight	KClO ₄ mg.
100	9.1
97	11.0
96	12.0
95	17.0
94	19.0
91	25.0

¹ Tietjens, Laboratorium-buch für die Kalindustrie, 2nd ed., 1924.TABLE XXII.¹—DENSITY OF MIXTURES OF ETHYL ALCOHOL AND WATER (grams per milliliter).

Per cent alcohol by weight	Temperature °C.				
	15°	20°	25°	30°	35°
50	0.91776	0.91384	0.90985	0.90580	0.90168
60	0.89523	0.89113	0.88699	0.88278	0.87851
65	0.88364	0.87948	0.87527	0.87100	0.86667
70	0.87187	0.86766	0.86340	0.85908	0.85470
71	0.86949	527	100	667	228
72	710	287	0.85859	426	0.84986
73	470	047	618	184	743
74	229	0.85806	376	0.84941	500
75	0.85988	564	134	698	257
76	747	322	0.84891	455	013
77	505	079	647	211	0.83768
78	262	0.84835	403	0.83966	523
79	018	590	158	720	277
80	0.84772	344	0.83911	473	029
81	525	096	664	224	0.82780
82	277	0.83848	415	0.82974	530
83	028	590	164	724	279
84	0.83777	348	0.82913	473	027
85	525	095	660	220	0.81774
86	271	0.82840	405	0.81965	519
87	014	583	148	708	262
88	0.82754	323	0.81888	448	003
89	492	062	626	186	0.80742
90	227	0.81797	362	0.80922	478
91	0.81959	529	094	655	211
92	688	257	0.80823	384	0.79941
93	413	0.80983	549	111	669
94	134	705	272	0.79835	393
95	0.80852	424	0.79991	555	114
96	566	138	706	271	0.78831
97	274	0.79846	415	0.78981	542
98	0.79975	547	117	684	247
99	670	243	0.78814	382	0.77946
100	360	0.78934	506	075	641

¹ Abridged from the Smithsonian Physical Tables.

The concentration of the alcohol in alcohol-water mixtures is most easily obtained by determining the specific gravity with a hydrometer or

pycnometer. The latter method is more accurate. It is necessary to know the temperature at which the specific gravity is determined. Table XXII gives the density of alcohol of various percentages by weight at five temperatures. Special hydrometers, graduated in per cent alcohol, which simplify the determination, may be purchased.

PERCHLORATE METHODS

Owing to the great cost of platinum chloride, analysts have sought for a reagent of a cheaper nature and yet capable of forming an insoluble compound with potash. Perchloric acid is the reagent most widely used at the present time. The principle upon which the method is based is the insolubility of potassium perchlorate in strong alcohol containing a little perchloric acid and the comparatively easy solubility of the other bases usually associated with potassium in water.

The process was first proposed by Serullas¹ and prominently called to the attention of analysts by Schloesing,² Kraut³ and Bertrand.⁴ The method was fully developed by the French agricultural chemists in 1887.

In view of the difficulty experienced in determining potash and soda, or rather the chlorides of potash and soda, by means of chloroplatinic acid, Schloesing proposed the use of perchloric acid, stating that it was first suggested by Serullas, who was negligent in not citing in his paper the results of his work. The chief cause of the failure of the method proposed by Serullas was the difficulty of getting perchloric acid in sufficient quantities and in a pure state. Since a satisfactory and cheap supply of pure perchloric acid no longer stands in the way of the success of the method, it is now used extensively in the various official and trade laboratories of Europe. It has, however, not attained more than a very limited use in the United States.

The procedure of Schloesing and Wense⁵ depends upon the insolubility of potassium perchlorate and the solubility of sodium perchlorate in 97 per cent alcohol. Ammonium salts and sulfates must not be present on account of their slight solubility in alcohol, but a little phosphate does no harm. The method follows:

¹ *Ann. chim. physique*, **46**, (2), 294 (1831).

² *Compt. rend.*, **73**, 1269 (1871).

³ *Z. anal. Chem.*, **14**, 152 (1875).

⁴ *Mon. sci.*, **23**, 961 (1881).

⁵ Treadwell and Hall, *Analytical Chemistry*, 5th ed.; *Z. angew. Chem.*, **4**, 691 (1891); **5**, 233 (1892); **6**, 68 (1893); *Landw. Vers. Sta.*, **59**, 313 (1903-4); **67**, 145; *J. Am. Chem. Soc.*, **36**, 2085 (1914).

When the solution to be analyzed contains sulfate, acidify with 10 cc. of 12 *N* hydrochloric acid, heat to boiling and treat drop wise with boiling 0.5 *N* barium chloride solution until no more precipitate is formed. Boil the solution gently for 15 minutes and filter. (This treatment is unnecessary when only a trace of sulfate is present, and in all cases an excess of barium chloride should be avoided.) Evaporate the solution to dryness in platinum and expel any ammonium salts by careful ignition. Dissolve the residue in 20 cc. of hot water and add a little more than enough perchloric acid to combine with all the bases present. (1 cc. of 20 per cent perchloric acid is sufficient for 50 mg. of potassium.) Evaporate the solution to dryness, dissolve the residue in 10 cc. of hot water, add a little more perchloric acid, and repeat the evaporation to dryness. If white fumes of perchloric acid do not appear, repeat the addition of water and the acid until finally heavy fumes are obtained on evaporation. After cooling, treat the residue with about 20 cc. of 0.2 per cent perchloric acid in 97 per cent alcohol. Break up the crystals somewhat, but take care not to reduce them to a fine powder which will subsequently pass through the filter. Decant the solution through a Gooch crucible, which has been washed with the 0.2 per cent solution of perchloric acid in alcohol, dry at 130° C., and weigh. If there is an unusually large precipitate of potassium perchlorate, dissolve it in a little hot water and again evaporate the solution with a little perchloric acid. Then wash the precipitate once by decantation with 0.2 per cent perchloric acid in alcohol and then several times on the asbestos felt. (The small quantity of perchloric acid remaining will be volatilized during the drying.) Finally dry the crucible and its contents at 130° C. for 1 hour and weigh.

In discussing the estimation of potassium in fertilizers, soil extracts and plant ashes, W. A. Davis¹ claims that the perchloric acid method is simpler and more reliable than the platinum method. He advocates washing the precipitate with 95 per cent alcohol saturated with potassium perchlorate, by means of which the error due to the solubility of the precipitate is obviated. (This is of great importance when precipitates of small weight are considered.) The presence of barium, magnesium and calcium chlorides and sodium phosphate are without prejudice to the method, and these salts need not be removed. The author also claims that potash in potassium sulfate can be determined without previous conversion into the chloride by using sufficient excess of perchloric acid. If the sulfate is converted into chloride with barium chloride by the Stassfurt method, exact precipitation of the sulfate radical is not necessary. Thin and Cumming² concur with Davis in his recommendation as to the use of 95-96 per cent alcohol saturated with pure perchloric acid in washing potassium perchlorate precipitates. They further state that ammonium salts must not be present in any quantity. Evaporation with the perchloric acid must be carried far enough to ensure complete conversion of chlorides

¹ *J. Agr. Sci.*, **5**, 52 (1912).

² *J. Chem. Soc. Trans.*, **107**, 361 (1915).

into perchlorates, and a freshly prepared saturated solution of potassium perchlorate must be used as a washing liquid.

Davis¹ also notes certain precautions that must be observed in carrying out the perchloric acid method. In evaporating potassium sulfate with perchloric acid, the conversion of the potassium into perchlorate proceeds quantitatively so long as the perchloric acid remains in a relatively large excess. On continuing the evaporation, however, with resultant expulsion of the greater portion of the perchloric acid, the less volatile sulfuric acid, which remains, causes reversal of the reaction. Under such conditions, upon the addition of 95 per cent alcohol an impure perchlorate, containing crystals of hydrated potassium hydrogen sulfate, separates. When dried at 100° C., such a precipitate gives a slightly high result owing to the presence of water of hydration. Although it is claimed by the author that potassium, even in the form of sulfate, can be accurately determined in the presence of an excess of perchloric acid, it is recommended that the sulfate be eliminated by evaporating the solutions with barium hydroxide solution, gently igniting well below the red heat, and using the filtered aqueous extract for evaporation with perchloric acid.

Page² gives results of investigations showing that chloric acid is often present in the perchloric acid and causes erroneous and erratic results. Perchloric acid, therefore, should be tested for the presence of chloric acid.

Bennett,³ while recognizing the existence of possible sources of error in both the cobaltinitrite and perchlorate methods for the determination of potassium, proposes the following combination of the two methods, which makes possible an accurate estimation even in the presence of relatively large quantities of sodium and magnesium salts.

To prepare the cobalt solution, dissolve 50 grams of cobalt nitrate in water, add 25 grams of glacial acetic acid and dilute to 1 liter. Allow the solution to stand 24 hours and filter.

Add 30 cc. of this solution to every 50 cc. of the potassium salt solution, allow to stand 2 hours, filter by the aid of suction and wash with water containing a small quantity of the cobalt reagent. Dissolve the precipitate in hot hydrochloric acid, filter the solution, and evaporate to dryness in a porcelain dish. After dissolving the residue in hot water, add perchloric acid and evaporate the solution to dryness. Cool, treat the residue with 25 cc. of 98 per cent alcohol, stir well, and bring upon a Gooch filter; wash with alcohol saturated with potassium perchlorate and containing 2 per cent perchloric acid, dry at 100° C., and weigh. The method cannot be used in the presence of ammonium salts.

¹ *J. Chem. Soc.*, **107**, 1678 (1915).

² *J. Agr. Sci.*, **14**, 133 (1924).

³ *Analyst*, **41**, 165 (1916).

Gooch and Blake¹ report that the use of an alcoholic wash solution saturated with potassium perchlorate results in the precipitation of some of the latter from solution when sodium perchlorate is present. Accordingly they dissent from the recommendation of Davis regarding the use of this wash solution, stating that it is practicable to so restrict the volume of the washing liquid (97 per cent alcohol containing 0.1 per cent of perchloric acid) that the solubility of the precipitated perchlorate is insignificant for practical purposes. The employment of the first filtrate to aid in effecting the transfer of the precipitate from the evaporating dish to the filter makes possible an economy in the use of the alcoholic wash solution.

Gooch and Blake further state that when a large quantity of alkali chlorides (*e. g.*, 0.3 gram) is present, a single evaporation with a moderate excess of perchloric acid is not sufficient for the complete conversion of such salts, but that the residue from the first evaporation with perchloric acid should be dissolved in the least possible quantity of water, another portion of perchloric acid added, and the evaporation repeated.

Although supporting the original suggestion of Davis² for the employment of wash alcohol saturated with potassium perchlorate, Baxter and Kobayashi³ agree with the contention of Gooch and Blake that potassium perchlorate may be precipitated from the wash liquor when large quantities of sodium are present. These writers recommend—

(1) The use of absolute alcohol; (2) The use of a low temperature in washing (0°); (3) The use of a platinum sponge crucible; (4) At least one solution of the precipitate in water and re-evaporation before the final washing; (5) The use of a washing liquor already saturated with potassium perchlorate, a suitable proportion of the salt being dissolved in alcohol at a high temperature before the perchloric acid is added.

Hager and Kern⁴ recommend the use of alcohol of at least 96 per cent strength by volume and containing as much as 1 per cent of perchloric acid for washing the perchlorate precipitate in the higher grade potassium salts. They found that as the strength of the alcohol wash solution was decreased, the solubility of the potassium perchlorate was increased. The low results obtained in the estimation of potassium in samples high in sul-

¹ *Am. J. Sci.*, [4], **44**, 381 (1917).

² *J. Agr. Sci.*, **5**, 52 (1912).

³ *J. Am. Chem. Soc.*, **39**, 249 (1917).

⁴ *Landw. Vers. Sta.*, **67**, 365 (1915); *J. Chem. Soc.*, **110**, pt. 2, 114 (1916).

fates are ascribed to the occlusion of potassium salts by the barium sulfate formed in the removal of sulfates from solution.

Hüttner¹ proposes the substitution of barium bromide, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$, for barium chloride for use in precipitating sulfates in the perchlorate method, because the barium bromide is soluble in alcohol. A solution of the bromide should give no precipitate upon the addition of alcohol.

A highly concentrated solution of barium bromide in water is added in excess to a cold solution of the potassium salt, and after thorough mixing the contents are made up to the mark. After settling, the precipitate is filtered, and 10 cc. of the filtrate is treated with perchloric acid. Solution in cold water can usually be followed, but in case carnallite leaves an insoluble residue containing potassium, solution in the hot solvent must be resorted to. Hydrobromic acid must be used instead of hydrochloric acid to obviate formation of barium chloride.

Morris² commends the accuracy of the perchlorate method as compared with the platinum method. He states that two evaporations with perchloric acid should be made; if an excess of perchloric acid is present at the end of the first evaporation, the second evaporation will suffice. At least one solution of the precipitate, followed by re-evaporation, is necessary, after preliminary extraction with wash liquid, when sodium or other bases are present. Otherwise the results may be too high. With the use of 100 cc. of 97 per cent alcohol containing 0.2 per cent perchloric acid, he reports relatively small losses from washing the perchlorate precipitates, an average loss of 0.0016 gram per 0.640 gram of potassium perchlorate being noted at a temperature of 15° C., with a loss of 0.0021 gram at 19° C. By doubling the rapidity of filtration at 15° C., the loss of perchlorate was decreased one-fourth. By adding an equal volume of pure ether to the above solution, the loss of perchlorate on washing with 100 cc. of the ether mixture at 15° C. was reduced one-half.

Crotogino³ proposed two methods for the approximate determination of potash by the perchlorate method. In the first method a concentrated solution of the potassium salt is titrated with a 50 per cent sodium perchlorate solution, and the end point is determined by repeated trials, the precipitate being allowed to settle in each case. In the second method, a large excess of the sodium perchlorate solution is used, and the precipitated potassium perchlorate is brought onto a tared filter, washed with alcohol, dried at 140° C., and weighed.

¹ *Kali*, **12**, 178 (1918); *J. Chem. Soc.*, **114**, pt. 2, 454 (1918).

² *Analyst*, **45**, 349 (1920).

³ *Kali*, **8**, 332; *C. A.*, **8**, 3167 (1914).

The methods are rapid but only approximately accurate, since the results vary from 0.2 to 1 per cent.

Several workers have proposed methods using solvents other than ethyl alcohol. Amyl alcohol was used by Gooch,¹ pyridine by Kahlenberg and Krauskopf,² isobutyl alcohol by Winkler,³ ether and alcohol by Palkin,⁴ *n*-butyl alcohol by Willard and Smith,⁵ and also by Smith.⁶ Smith proposed a precipitation process, whereas nearly all other methods are extraction processes. The procedure consists in the precipitation of potassium perchlorate from its solution in warm water, in the presence of sodium perchlorate, by the slow addition of a proportionately large volume of *n*-butyl alcohol containing 0.5-1 per cent of perchloric acid dihydrate. The solution, together with the precipitated potassium perchlorate is then boiled for 30 seconds, cooled to room temperature, and filtered through a Gooch or Monroe crucible. The precipitate is washed with butyl alcohol, dried at 150-250° for ½-1 hour, and weighed as potassium perchlorate. Good results were obtained.

G. F. Smith⁷ and Smith and Ross⁸ made an exhaustive and critical study of the perchlorate method. The following discussion is based on their findings.

Potassium perchlorate crystallized from water solution can only be freed from water by drying at 350°; when dried at 150° it may retain 0.3 per cent of water by weight. Half of this is removed by drying at 250°.

The evaporation of water solutions of perchloric acid results in concentration of the acid to approximately the constant boiling aqueous acid of 72.5 per cent strength. Potassium perchlorate occludes perchloric acid when precipitated from 72.5 per cent acid and this occluded acid is not completely removed by heating at 350° for 30 minutes. This occlusion was found to be independent of the nature of the organic solvent used in washing.

Errors due to occlusion are offset, often quite satisfactorily, by the solubility of the potassium perchlorate in the solvents used in the ordinary methods. When an improved solvent is used, *e. g.*, ethyl acetate, the errors due to occlusion appear to be augmented.

¹ *Am. Chem. J.*, **9**, 33 (1887).

² *J. Am. Chem. Soc.*, **30**, 1104 (1908).

³ *Z. anal. Chem.*, **52**, 628 (1913).

⁴ *J. Am. Chem. Soc.*, **38**, 2326 (1916).

⁵ *Ibid.*, **44**, 2816 (1922).

⁶ *Ibid.*, **45**, 2073 (1923).

⁷ *Ibid.*, **47**, 762-769 (1925).

⁸ *Ibid.*, 774-81, 1020-1026.

As the result of these studies on occlusion and an exhaustive study of solvents for washing the perchlorate precipitate, Smith and Ross recommend the following procedure.

Dissolve the mixed chlorides of potassium, sodium and lithium free from ammonium salts, as obtained by the J. Lawrence Smith or other method, in water and treat with 2-3 times the equivalent quantity of perchloric acid (not less than 1 cc. of 60-70 per cent acid). Evaporate to dryness in a 150 cc. Pyrex beaker on a hot plate. (The temperature must be high enough to cause the solution to fume. The beaker and contents should be dry and any acid condensed on the walls of the beaker should be removed by brushing with a free flame.) Cool the beaker sufficiently, dissolve the contents by adding 2-3 cc. of hot water, and evaporate again on the hot plate. Cool the beaker, add 10-20 cc. of a mixture of equal parts by volume of *n*-butyl alcohol and ethyl acetate and digest near the boiling point for 2-3 minutes. Cool the solution to room temperature, decant the supernatant liquid through a previously ignited and weighed Munroe crucible, and wash three times by decantation to remove most of the soluble perchlorates. Dissolve the residue in the minimum of hot water and again evaporate to dryness. Extract the salts as before, using 10 cc. of solvent; digest the liquid, cool, and filter into the original crucible. Transfer the precipitate to the crucible, using a fine jet from a wash bottle containing the same solvents used for the extraction, and wash the crucible 10-15 times with 0.5-1 cc. portions from the wash bottle. Dry the original beakers on the hot plate and brush any unremoved particles of perchlorate in with the bulk of the precipitate. Dry the precipitate and crucible for a few minutes in an oven at 110° C. and finally for 15 minutes in a muffle at 350°. Cool and weigh.

The volume of filtrate and washings used in this procedure should be 35-40 cc. Since it was found under actual working conditions that the solubility of potassium perchlorate in the solvent used was only 1.0 mg. in 100 cc., corresponding to 0.6 mg. of potassium chloride or 0.34 mg. of K_2O , it is evident that the error introduced by this factor is very slight. Gooch crucibles with asbestos mats may be used instead of the Monroe crucibles.

It will be noted that this procedure, which is recommended for very accurate work, does not involve the use of any organic solutions containing perchloric acid. Any remote danger of explosion resulting from such solutions is thus eliminated.

Kirzirian¹ departs from the usual procedure and precipitates potassium perchlorate by adding aniline perchlorate in alcoholic solution dropwise to the mixed chlorides dissolved in water.

Perchloric Acid.—A solution of perchloric acid in water containing about 20 per cent $HClO_4$ is the strength generally used in potassium determi-

¹ *Proc. Iowa Acad. Sci.*, **24**, 547 (1917).

nations. It must contain no substances that are insoluble in the wash alcohol used or that react with other materials present to produce such insoluble substances. In general the acid will be suitable for use if it gives no turbidity with barium chloride or when 10 cc. of alcohol is added to 10 cc. of the acid.

Perchloric acid of satisfactory purity can now be purchased or the acid may be prepared. Water solutions of perchloric acid as used in potassium determinations are not dangerous, but the anhydrous acid must be carefully handled to avoid explosions in the presence of organic matter.

(1) *Properties of Perchloric Acid.*¹—Anhydrous perchloric acid is a colorless, hygroscopic, volatile, mobile liquid, which fumes in the air. When the anhydrous acid comes in contact with the skin, it produces serious and painful wounds. D. Vorlander and R. von Schilling² say that the pure acid decomposes spontaneously in a few weeks even in the dark and that the liquid first darkens in color and then explodes, while A. Michael and W. T. Conn³ say that it does not explode.

Perchloric acid readily unites with water to form needle-like crystals of the monohydrate, which was mistaken by Serullas⁴ (1831) for the anhydrous acid. The solution of the acid in water is much more stable since it decomposes neither in light nor in darkness if organic matter and reducing agents be excluded. It cannot be too strongly emphasized that contact of the boiling undiluted acid or hot perchloric acid vapor with organic matter or even easily oxidized inorganic matter, such as compounds of trivalent antimony, will lead to serious explosions.⁵

The specific gravity of 100 per cent acid is found by Van Wijk⁶ to be 1.7676 at 20° C.

(2) *Preparation of Perchloric Acid.*⁷—Kreider worked out the following simple method of preparing perchloric acid:

A convenient quantity of sodium chlorate, 100–300 grams, is melted in a glass retort or round-bottom flask and gradually raised to a temperature at which oxygen is freely, but not too rapidly evolved; it is kept at this temperature until the fused mass thickens throughout, indicating the complete conversion of the chlorate to the chloride and perchlorate, which requires from 1½–2 hours; or the retort may be connected with a gasometer and the end of the reaction determined by the volume of

¹ Mellor, *Inorganic and Theoretical Chemistry*, Vol. II, p. 376.

² *Liebig's Ann.*, **310**, 369 (1900).

³ *Am. Chcm. J.*, **23**, 445 (1900).

⁴ *Ann. chim. phys.*, **46**, 294 (1831).

⁵ Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 37, 1929.

⁶ *Z. anorg. Chem.*, **32**, 115 (1902).

⁷ *Am. J. Sci.*, [3], **49**, 443 (1895).

oxygen expelled, as represented in the equation— $2\text{NaClO}_3 = \text{NaCl} + \text{NaClO}_4 + \text{O}_2$. The product thus obtained is washed from the retort to a capacious evaporating dish, where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which will be present in but small amount, if the ignition has been carefully conducted with well distributed heat. It is then evaporated to dryness on the steam bath, or more quickly over a direct flame; but little attention is necessary until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilization of the remaining liquid and in breaking up the mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water, and its removal from the dish, without moistening and reheating, is impossible.

After triturating the residue in a porcelain mortar an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker, where there is less surface for the escape of hydrochloric acid and from which the acid can be decanted without disturbing the precipitated chloride. If the salt has been reduced to a very fine powder by energetic stirring for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chloride, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a Gooch crucible, and the residue is treated again with the strongest hydrochloric acid, settled, and again decanted, the salt finally being brought upon the filter, where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface. When the filter will not hold all the sodium chloride, the latter, after being washed, may be removed by water or by mechanical means, if precautions are taken not to disturb the felt, which is then ready for the remainder. If water is used, the felt should be washed with a little strong hydrochloric acid before receiving another portion of the salt. This residue will be found to contain only a small quantity of perchlorate. It may be tested by heating to expel the free acid and treating the dry and powdered residue with 97 per cent alcohol, which dissolves the perchlorate of sodium, but has little effect on the chloride.

The filtrate containing the perchloric acid, the excess of hydrochloric acid and the small percentage of sodium chloride which is soluble in the latter, is then evaporated over the steam bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for use in potassium determinations.

The acid will not be chemically pure, because sodium chloride is not absolutely insoluble in hydrochloric acid, but a portion tested with silver nitrate will prove that the sodium, together with any other bases which may have gone through the filter, has been completely converted into perchlorate. Then, unless the original chlorate contained some potassium or on evaporation the acid was exposed to the fumes of ammonia, the residue of the evaporation of a portion is easily and completely soluble in 97 per cent alcohol, and its presence, therefore, is unobjectionable.

TABLE XXIII.¹—DENSITY AND CONCENTRATION OF PURE AQUEOUS PERCHLORIC ACID AT 15°, REFERRED TO WATER AT 4°.

Density HClO ₄		Density HClO ₄		Density HClO ₄		Density HClO ₄		Density HClO ₄	
Per cent		Per cent		Per cent		Per cent		Per cent	
1.005	1.00	1.140	21.64	1.275	37.00	1.410	50.10	1.545	60.41
1.010	1.90	1.145	22.32	1.280	38.10	1.415	50.51	1.550	60.78
1.015	2.77	1.150	22.90	1.285	38.60	1.420	50.91	1.555	61.15
1.020	3.61	1.155	23.65	1.290	39.10	1.425	51.31	1.560	61.52
1.025	4.43	1.160	24.30	1.295	39.60	1.430	51.71	1.565	61.89
1.030	5.25	1.165	24.94	1.300	40.10	1.435	52.11	1.570	62.26
1.035	6.07	1.170	25.57	1.305	40.59	1.440	52.51	1.575	62.63
1.040	6.88	1.175	26.20	1.310	41.08	1.445	52.91	1.580	63.00
1.045	7.68	1.180	26.82	1.315	41.56	1.450	53.31	1.585	63.37
1.050	8.48	1.185	27.44	1.320	42.03	1.455	53.71	1.590	63.74
1.055	9.28	1.190	28.05	1.325	42.49	1.460	54.11	1.595	64.12
1.060	10.06	1.195	28.66	1.330	42.97	1.465	54.50	1.600	64.50
1.065	10.83	1.200	29.26	1.335	43.43	1.470	54.89	1.605	64.88
1.070	11.58	1.205	29.86	1.340	43.89	1.475	55.18	1.610	65.26
1.075	12.33	1.210	30.45	1.345	44.35	1.480	55.56	1.615	65.63
1.080	13.08	1.215	31.04	1.350	44.81	1.485	55.95	1.620	66.01
1.085	13.83	1.220	31.61	1.355	45.26	1.490	56.32	1.625	66.39
1.090	14.56	1.225	32.18	1.360	45.71	1.495	56.69	1.630	66.76
1.095	15.28	1.230	32.74	1.365	46.16	1.500	57.06	1.635	67.13
1.100	16.00	1.235	33.29	1.370	46.61	1.505	57.44	1.640	67.51
1.105	16.72	1.240	33.85	1.375	47.05	1.510	57.81	1.645	67.89
1.110	17.45	1.245	34.40	1.380	47.49	1.515	58.17	1.650	68.26
1.115	18.16	1.250	34.95	1.385	47.93	1.520	58.54	1.655	68.64
1.120	18.88	1.255	35.49	1.390	48.37	1.525	58.91	1.660	69.02
1.125	19.57	1.260	36.03	1.395	48.80	1.530	59.28	1.665	69.40
1.130	20.26	1.265	36.56	1.400	49.23	1.535	59.66	1.670	69.77
1.135	20.95	1.270	37.08	1.405	49.68	1.540	60.04	1.675	70.15

¹ Emster, *Z. anorg. Chem.*, **52**, 278 (1907).

One cubic centimeter of the acid thus obtained gives on evaporation a residue of only 0.036 gram, which is completely soluble in 97 per cent alcohol.

Willard¹ proposes the following method for the preparation of perchloric acid:

In a 2 liter flask place 500 grams of ammonium perchlorate, add 600 cc. of water and 410 grams of 68-70 per cent nitric acid, heat to boiling, and let 105 grams of 37 per cent hydrochloric acid, previously diluted to 400-500 cc., run in through a long stemmed dropping funnel. Run the acid in rapidly at first, then more slowly (all may be added within 25 minutes). Boil vigorously throughout the entire operation. Continue to boil for about 1 hour, running water in to replace that lost by evaporation to keep the volume constant and finally boil down the solution rapidly until fumes of perchloric acid appear.

¹ *J. Am. Chem. Soc.*, **34**, 1480-5 (1912).

The acid should now be free from ammonium as shown by Nessler's test. Usually there will be a slight excess of nitric acid, and this requires a somewhat higher temperature for its complete removal than does hydrochloric acid, where 135°C . suffices. It may in some cases be advisable to add a little more hydrochloric acid to react with the nitric acid present, leaving an excess of the former. A casserole or evaporating dish is more efficient in the last evaporation. When the acid fumes copiously, its composition is nearly that of the dihydrate $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, this being the constant boiling product obtained by distillation. The yield is theoretical—580 grams of the dihydrate—and the entire process may be easily completed within $2\frac{1}{2}$ hours.

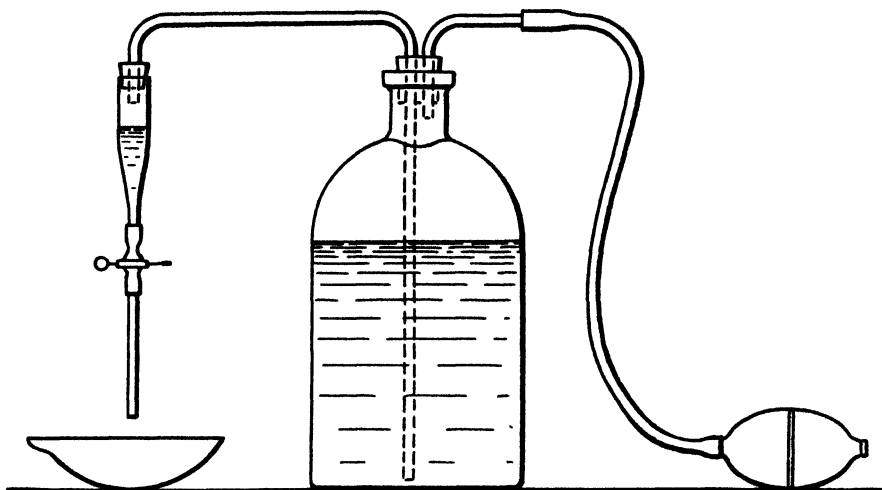


Fig. 3.—Perchloric Acid Container

The acid obtained in this way is easily purified by distillation, and this method will probably be the cheapest if a perfectly pure product is required. A pressure of 200 mm. is very satisfactory; at higher pressures decomposition becomes noticeable, until at atmospheric pressure a loss of perhaps 10 per cent is inevitable.

It will be found very convenient to keep the perchloric acid stock solution in an apparatus of the type shown in Fig. 3, which will automatically deliver the correct amount of acid for the determination. The small measuring tube at the side is equipped with a two-hole stopper, through one hole of which passes the tube from the bottle as shown. The other hole allows the air to escape. When the bulb is pressed, the acid fills the

measuring tube, and on releasing the bulb the excess flows back into the bottle. Obviously the quantity of acid retained in the measuring tube can be adjusted by sliding it up or down on the delivery tube from the bottle. The acid is allowed to flow into the evaporating dish by opening the pinch clamp. No dimensions are given as to the size of the bottle and measuring tube; they will depend on the needs of the individual analyst.

The concentration of pure aqueous perchloric acid solutions is conveniently obtained by determining the specific gravity.

VOLUMETRIC METHODS

BITARTRATE METHODS

Several of these methods are based upon the precipitation of the bitartrate in the presence of an excess of alcohol, but it is claimed by some workers in this field that by the use of sodium bitartrate or a mixture of solutions of sodium tartrate and tartaric acid, potassium bitartrate may be precipitated with approximately quantitative results.

Marchand¹ describes a method which has as its basis the diminution of acidity caused by the separation of insoluble potassium bitartrate from a mixture of sodium bitartrate with a neutral solution of a potassium salt. Precipitation is effected overnight, and the minimum temperature at which precipitation is accomplished is noted, correction for temperature being made for each determination by means of an empirical table.

In the method described by Bayer² a weighed quantity of potash salt is dissolved in water, an aliquot is taken, and sodium carbonate is added in small quantity, followed by a small proportion of acetic acid and an excess of crystallized tartaric acid. The solution is heated; after cooling, absolute alcohol is added in large amount and the liquid is allowed to stand several hours.

The precipitate, after being washed with alcohol, is titrated in a boiling solution of 0.05 *N* sodium hydroxide, phenolphthalein being used as an indicator. A correction is made for the potassium bitartrate soluble in the alcoholic wash water.

In the method described by Marshall³ the alkali metals should be present as chlorides, and if necessary they can first be converted into sulfates and then to chlorides by means of barium chloride. An aliquot por-

¹ *Ann. agron.*, **9**, 465; *J. Chem. Soc.*, **46**, 695 (1884).

² *Chem. Ztg.*, **17**, 686 (1893).

³ *Ibid.*, **38**, 585 (1914); *J. Chem. Soc.*, **106**, pt. 2, 490 (1914).

tion of a solution containing about 0.05 gram of potassium oxide is evaporated to dryness on the water bath. The residue is dissolved in a few drops of water and precipitated in the cold with 20 cc. of a 2 per cent alcoholic solution of tartaric acid which has been kept for several days over potassium bitartrate and then filtered. After precipitation, 10-20 cc. of 96 per cent alcohol saturated with potassium bitartrate is added, and the whole mixture is boiled for 10 minutes on the water bath, and then left covered with occasional shaking for 24 hours. The precipitate is collected in a Gooch crucible, washed with alcohol containing bitartrate then with 96 per cent alcohol, dried at 80° C., and weighed.

Ajon¹ reports good results for potassium chloride and sulfate by the following method:

Make 25 cc. of a 2 per cent potassium chloride or sulfate solution up to 150-200 cc. in an Erlenmeyer flask and add slowly and with stirring 50 cc. of 2 *N* tartaric acid and 25 cc. of 0.5 *N* sodium hydroxide solution. Shake the flask for 5 minutes and add 25 cc. of 96 per cent alcohol. After allowing to stand 6-8 hours, filter through a fine texture filter paper and wash well by decantation with neutral 96 per cent alcohol. Remove the filter paper from the funnel, place in the flask, and add 0.1 *N* sodium hydroxide until the contents react alkaline to phenolphthalein and retain a pink color for not less than 5 minutes. Dissolve the precipitate in aqueous 0.1 *N* sodium hydroxide and titrate the excess with 0.1 *N* hydrochloric acid.

St. Minovici and Kollo² describe a method which depends upon precipitation of potassium as bitartrate, but unlike similar methods it does not depend upon the use of alcohol to decrease the solubility of the bitartrate, nor is the presence of sodium, sulfate or phosphate ions objectionable. Experiments showed that the solubility of potassium bitartrate in a saturated solution of sodium bitartrate, or in the presence of excess tartaric acid that has been saturated with potassium salt, is inappreciable. Only 0.01 per cent dissolves in a 7.5 per cent solution and less in a saturated solution. For the analysis proceed as follows:

Dissolve 0.25-0.3 gram of the salt in 5 cc. of water, add 0.5-0.6 gram of sodium bitartrate and allow to stand 1 hour, with occasional stirring. Add 5 cc. of 5 per cent tartaric acid, which has been allowed to stand 5-6 days with 1 gram of potassium bitartrate for each 100 cc. of solution, and filter. Wash twice more by decantation with 5 cc. portions of tartaric acid to dissolve any excess of sodium bitartrate. Then wash on the filter with 50 cc. of a mixture of equal parts of alcohol and ether to dissolve excess of tartaric acid. The precipitate may be weighed or dissolved in boiling water and titrated with sodium hydroxide and phenolphthalein. To the

¹ *Giorn. chim. ind. applicata*, **2**, 422 (1920); *J. Soc. Chem. Ind.*, **40**, 21 A (1921).

² *Bul. soc. chim. România*, **3**, 17, 25 (1921); *C. A.*, **15**, 3044.

weight of potassium oxide found, add 0.005 gram in addition to allow for the solubility of potassium bitartrate.

The following modification of the method of Przibylla¹ is recommended by Hubert.²

Dissolve 20–25 grams of sample in 200–250 cc. of water, filter if necessary, and place a suitable aliquot in a dry flask; add a measured quantity of sodium bitartrate (Przibylla used tartaric acid), shake thoroughly for 5–20 minutes at a temperature of 18° C., filter, and titrate the filtrate with 0.1 *N* sodium hydroxide.

By analyzing a series of synthetic solutions that have the same composition as the various potassium salts to be analyzed, the relation between the final titration and the percentage of potassium oxide can be determined for each of the salts.

In a later paper Przibylla³ recommends the use of rosolic acid instead of phenolphthalein, as first recommended. He notes that in the original paper results were obtained with 10 per cent potassium salt solutions, sodium bitartrate being used as precipitant without a mechanical stirrer.

Hubert⁴ later gives another modification of the Przibylla method as follows:

Dissolve 25 grams of the salt in water and dilute the solution to 250 cc. in a graduated flask at 18° C. Transfer a 25 cc. aliquot to a dry 200 cc. flask, add the necessary amounts of sodium tartrate and tartaric acid, shake in a water bath for 20 minutes, and then filter through a dry paper. Titrate a definite quantity of filtrate with 0.1 *N* sodium hydroxide solution (free from carbonate), using rosolic acid as an indicator, and read off the percentage of potassium on a curve previously constructed from results obtained from standard preparations.

Tables are given by the author showing amounts of reagents taken, which vary according to richness of samples analyzed.

The following procedure is recommended by Meurice.⁵

To a quantity of potash salt corresponding to 0.65 gram in 20–25 cc. of water, add 100 cc. of saturated solution of sodium bitartrate and an equal volume of methyl alcohol (used because cheaper than ethyl alcohol in France). Allow to stand overnight. Wash the precipitate with 50 per cent methanol, dissolve in a little water, and titrate with sodium hydroxide and phenolphthalein. Sulfate, nitrate, calcium and magnesium ions do not interfere. In new hands it is claimed that better results are obtained than are secured by the perchloric acid method.

¹ *Kali*, **2**, No. 18, (1908); *C. A.*, **7**, 2024.

² *Bull. soc. ind. Mulhouse*, **88**, 500 (1922).

³ *Kali*, **6**, 473 (1912); *C. A.*, **7**, 2024.

⁴ *Ann. chim. anal.*, [2] **5**, 9 (1923); *J. Chem. Soc.*, **124**, pt. 2, 181 (1923).

⁵ *Ann. chim. anal. chim. appl.*, **7**, 161 (1925); *C. A.*, **19**, 2613..

The following bitartrate method was proposed by Macheleidt.¹

Prepare a standard solution of sodium bitartrate by dissolving 60 grams of tartaric acid and 16 grams of sodium hydroxide in water and diluting to 1 liter. Add 6 grams of potassium bitartrate to the solution and shake the liquid for 2 hours; filter off 30 cc. and titrate with 0.1 *N* barium hydroxide solution. Shake a second portion of 30 cc. for 1–2 hours with 0.5–0.75 gram of sample to be tested. Filter the solution into a tared basin, and without washing the filter titrate with barium hydroxide solution. Weigh the solution before and after filtering, and make allowance for the loss. Calculate the difference between the two titrations to potassium oxide.

PHOSPHOMOLYBDATE METHODS

Raulin² apparently was the first to propose a method based upon the insolubility in water of potassium phosphomolybdate, and some years later Wavelet³ described a method for the determination of potash by means of phosphomolybdic acid. The potash is precipitated as phosphomolybdate, being evaporated to dryness on the water bath, and after being washed with dilute nitric acid, is dissolved in ammonia and precipitated by means of magnesia mixture. The author also proposed the titration of the ammonium magnesium phosphate with lead nitrate.

The modified method of Donk⁴ for the determination of potash volumetrically is as follows:

REAGENTS

Nitric acid wash.—5.5 cc. of nitric acid, (sp. gr. 1.40), in 1000 cc. of water.

Sodium nitrate wash.—5 grams of sodium nitrate in 1000 cc. of water.

Phosphomolybdic acid solution.—Dissolve 100 grams of phosphomolybdic acid (Kahlbaum) in 750 cc. of water and add 250 cc. of nitric acid, (sp. gr. 1.40).

Standard solutions.—Prepare standard caustic potash and nitric acid as for the volumetric determination of phosphoric acid, (p. 174). 1 cc. of potassium hydroxide is equal to 1.625 mg. of potassium oxide.⁵

DETERMINATION

Boil 2 grams of the sample 30 minutes with 300 cc. of water plus 5 cc. of concentrated hydrochloric acid. Add a few drops of phenolphthalein and carefully

¹ *Wochschr. Brau.*, **39**, 23 (1922).

² *Compt. rend.*, **110**, 289 (1890); *Ann. chim. anal.*, **5**, 345 (1900); U. S. Dept. Agr. Bur. Chem. Bull., **90**, 219.

³ *Ann. chim. anal. appl.*, **5**, 289 (1900); *Chem. Centbl.*, **II**, 689 (1900); *Exp. Sta. Rec.*, **12**, 713 (1900-1).

⁴ U. S. Dept. Agr. Bur. Chem. Bull., **99**, p. 135 (1906).

⁵ The factor originally used was 1.655 but the correct factor is 1.625 according to McDonnell, U. S. Dept. Agr. Bur. Chem. Bull., **99**, p. 140.

neutralize with caustic soda, avoiding an excess. (A 10 per cent sodium hydroxide solution free from potash is used.) Precipitate the lime with ammonium oxalate, make up to 500 cc., filter, evaporate a 25 cc. aliquot to dryness, and ignite to destroy ammonium salts. Dissolve the residue from the ignition, transfer to a porcelain dish, add 10 cc. of phosphomolybdic solution, and evaporate to dryness. Add 25 cc. of nitric acid wash heated to 50° C., allow the solution to cool, filter through an asbestos filter, and wash with sodium nitrate wash. Transfer to an Erlenmeyer flask, add an excess of standard potassium hydroxide, and heat nearly to boiling. Wash into the flask with the standard alkali any precipitate adhering to the dish. When the precipitate is completely dissolved, add a few drops of phenolphthalein, and titrate back with standard nitric acid.

Schlicht¹ claims that more satisfactory results are obtained by washing the precipitate with 5 per cent solution of magnesium sulfate, then with a solution of ammonium nitrate, and finally with alcohol and ether.

COBALTINITRITE METHODS

A cobaltinitrite method was used for the qualitative detection of potassium many years before it was used for the quantitative estimation of this element, de Koninck² being credited with suggesting the use of this reagent, to which his name has been given, although almost simultaneously Curtman proposed the employment of the same reagent for the detection of potassium.³ Its use in the quantitative determination of potassium was first proposed by Gilbert,⁴ who gave the formula of the precipitated triple salt as $\text{Co}(\text{NO}_2)_3 + 3(\text{KNa})\text{NO}_2 + n\text{H}_2\text{O}$. Weber⁵ stated that it was impracticable to apply this method gravimetrically owing to the variable water content of the precipitate, but proposed to precipitate the potassium by the cobaltinitrite method, dissolving the precipitate in hydrochloric acid and completing the determination either by the perchlorate or the chloroplatinate method (compare the British official methods, p. 429). Closely agreeing results of the two modifications of the method are reported. About two years later the use of this method in the quantitative estimation of potassium was proposed by Adie and Wood,⁶ who called attention to the observations of Erdmann⁷ and Sadtler⁸ regarding double potassium

¹ *Chem. Ztg.*, **32**, 1125, 1138 (1908); *C. A.*, **3**, 410 (1909).

² *Z. Chem.*, **20**, 390 (1881); *Ber.*, **14**, 1951 (1881).

³ *Ber.*, **14**, 2298 (1881).

⁴ Inaug. dissertation, Tübingen, 1898.

⁵ *Z. anal. Chem.*, **83**, 171 (1899).

⁶ *J. Chem. Soc. Trans.*, **77**, 1076 (1900).

⁷ *J. Pr. Chem.*, **37**, 385 (1866).

⁸ *Am. J. Sci.*, [2] **49**, 189 (1870).

and cobaltinitrites precipitated by the addition of a strong solution of potassium and sodium nitrites to solutions of cobalt salts. These authors had also noted the fact that a solution of sodium cobaltinitrite (de Koninck's reagent) had been successfully used as a qualitative test for potassium, and their own experience with that reagent led them to a study of the possibility of developing a method for the quantitative determination of potassium.

The analysis of several samples of the precipitate obtained as a result of the above reaction showed the salt in question to be monohydrated dipotassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6 \cdot H_2O$. The preparation of the reagent was as follows:

Dissolve 113 grams of cobalt acetate in 300 cc. of water and 100 cc. of acetic acid; also dissolve 220 grams of sodium nitrite in 400 cc. of water. Filter the solutions and mix, and remove the nitric oxide by evacuation (with pump). After allowing to stand 24 hours, filter off the yellow precipitate that has separated, and make the solution up to a liter.

In determining potash in potash salts, the method proposed is as follows:

Weigh out 10 grams of muriate or sulfate of potash, or 40 grams of kainite, and dissolve in water, making the solution up to 1 liter. Filter off a portion through a dry filter, take 10 cc., add 10 cc. of the sodium cobaltinitrite reagent and 1 cc. of acetic acid, allow to stand until the precipitate has settled, pass through a Gooch filter and wash. Blow the precipitate and the asbestos plug out of the Gooch filter into a beaker and boil with sodium hydroxide solution. Filter off the asbestos and precipitated hydroxide and make up the filtrate containing all the nitrite of the precipitate to 100 cc. Acidify 20 cc. of the solution and titrate rapidly with 0.1 *N* potassium permanganate solution. Make a second titration, adding the same volume of permanganate before acidification as was used in the first titration, and completing the titration after addition of excess of acid.

The authors also recommend the method as a gravimetric process, the precipitate obtained as in the volumetric method being allowed to stand overnight, filtered either through a weighed Gooch filter or weighed filter paper, washed with 10 per cent acetic acid until the washings are colorless, and finally once with water, dried at 125° C. until the weight is constant, and weighed.

Some years later Drushel¹ called attention to the possibility of so modifying this process as to remove certain difficulties attendant upon the original method of Adie and Wood.

¹ *Am. J. Sci.*, [4] **24**, 433 (1907).

It was noted by Drushel that "unless the potassium salt is of proper concentration the precipitate is very difficult to filter and wash, and shows a tendency to pass through the mat. By repeated experiments it was found that this difficulty, as well as the necessity for allowing the precipitate to stand overnight, is avoided by evaporating the mixture nearly to dryness on the steam bath after adding the sodium cobaltinitrite solution in considerable excess." A further change in the method was made by obviating the preliminary decomposition of the precipitate and removal of the cobalt as recommended by Adie and Wood, oxidation with permanganate being effected directly, while standard oxalic acid was then added in excess, followed by titration to color with permanganate.

The details of Drushel's modified process are as follows:

The solution of a potassium salt, containing not more than 0.2 gram of potassium oxide and free from ammonium salt, is treated with a rather large excess of sodium cobaltinitrite solution acidified with acetic acid, and evaporated to a pasty consistency over the steam bath. It is then cooled and treated with 50-100 cc. of cold water and stirred until the excess of sodium cobaltinitrite is dissolved. It is allowed to settle and decanted through a perforated crucible fitted with an asbestos mat. The precipitate is washed two or three times by decantation, after which it is transferred to the crucible and thoroughly washed with cold water. In the meantime a measured excess of standard 0.1 *N* potassium permanganate is diluted to ten times its volume and heated nearly to boiling. Into this the precipitate and mat are transferred and stirred up, after which the crucible is also put into the solution, since particles of the precipitate stick persistently to the sides of the crucible. After the oxidation proceeds five or six minutes manganese hydroxide separates out and the color of the solution darkens. At this point 5-25 cc. of sulfuric acid (1 + 7) is added, and the solution, after stirring, is allowed to stand a few minutes. Then a measured amount of standard oxalic acid, containing 50 cc. of strong sulfuric acid per liter, is run in from a buret, care being taken to add an excess. The temperature is maintained a little below the boiling point until the solution becomes colorless and the manganese hydroxide has completely dissolved. It is then titrated to color by permanganate in the usual manner.

From the whole amount of permanganate used the permanganate equivalent of the oxalic acid used is subtracted and the remainder multiplied by the factor calculated for the strength of permanganate used, 0.000856 being the factor for strictly 0.1 *N* potassium permanganate.

To make the 0.1 *N* oxalic acid solution, exactly 7.1066 grams of pure recrystallized ammonium oxalate is dissolved in about 700 cc. of cold distilled water contained in a liter flask. To this solution is then added 50 cc. of strong sulfuric acid, and the contents of the flask are cooled to 15° C. and made up to the mark with distilled water.

Bowser¹ recommends the evaporation of the solution, after the addition of the reagent, to a sirupy consistency, though too vigorous heating is to be

¹ *J. Ind. Eng. Chem.*, **1**, 791 (1909).

avoided. The washed precipitate is treated in a beaker with an excess of standard permanganate, and the contents are boiled, rather than heated nearly to boiling, as in the original Drushel method.

In discussing the composition of the product obtained by the interaction of solutions of potassium salts and of sodium cobaltinitrite, Cunningham and Perkin¹ claimed that if the potassium salt was in excess tri-potassium cobaltinitrite ($K_3Co(NO_2)_6$) was precipitated, whereas with an excess of sodium cobaltinitrite, di-potassium sodium cobaltinitrite ($K_2NaCo(NO_2)_6$) was formed. If neither salt is in considerable excess, a mixture of the two salts is frequently obtained.

McDougall² calls attention to the variation in the factor used in the cobaltinitrite method for the determination of potash when the precipitate of potassium cobaltinitrite is dissolved in dilute sulfuric acid prior to addition of standard oxalic acid and titration with 0.1 *N* permanganate. According to Drushel's method, in which the precipitate is brought directly in contact with the hot diluted permanganate, 1 cc. of the permanganate is equal to 0.000856 gram of potash (K_2O), but when the procedure suggested by McDougall is followed, each cubic centimeter of the permanganate is equivalent to 0.000785 gram of potash. His explanation of the difference in the oxidizing value of the permanganate under the two conditions mentioned is that in an acid solution trivalent cobalt is not an active oxidizer and that in sulfuric acid solution the cobaltic salt formed must change in the cobaltous salt with evolution of free oxygen.

Mitscherlich and Fischer,³ as a result of investigations regarding the constitution of the precipitate of potassium sodium cobaltinitrite, state that the composition of the precipitate changes with the concentration of the reagent. With increasing proportions of the cobaltinitrite reagent the quantity of sodium entering the molecule of the product increases at the expense of the potassium. If the excess of the reagent amounts to thirty or more times as much sodium as potassium, the variations in composition of the precipitate fall within the limits of error of the estimation. The method, therefore, gives satisfactory results provided a large excess of precipitating reagent is used. The authors report good results from the use of the method in the estimation of potash in fertilizers.

The cobaltinitrite method of Mitscherlich and Fischer is reported by Christensen and Feilberg⁴ to give unsatisfactory results. In order to

¹ *J. Chem. Soc. Trans.*, **95**, 1563 (1909).

² *J. Am. Chem. Soc.*, **34**, 1684 (1912).

³ *Landw. Vers. Sta.*, **78**, 75 (1912); *Analyst*, **37**, 588 (1912).

⁴ *Landw. Vers. Sta.*, **97**, 27 (1920); *C. A.*, **15**, 1959.

secure a more complete and satisfactory precipitation these authors propose to add, along with the precipitating reagent, 5 cc. of a saturated solution of sodium chloride. The method thus modified should be applicable both to fertilizers and soil extracts.

Shedd¹ and others note the difficulty of preserving the sodium cobalt-nitrite solution unchanged and recommend the separate addition of the components of the solution. This recommendation was adopted by E. L. Baker, the Referee on Potash for the A. O. A. C. in 1911.² The method of preparation of these solutions was as follows:

Sodium nitrite solution.—Dissolve 220 grams of sodium nitrite in water and dilute to 500 cc.

Cobalt acetate solution.—Dissolve 113 grams of cobalt acetate in about 300 cc. of water, add 100 cc. of glacial acetic acid, and dilute to 500 cc.

Sodium cobaltinitrite solution.—Mix equal parts of the sodium nitrite and cobalt acetate solutions a few hours before required for use. A yellow precipitate forms on standing. Filter just before using.

Standard solutions.—0.2 *N* potassium permanganate and 0.2 *N* oxalic acid solution; solutions of fertilizers to be made up by the official method. The factor for 0.2 *N* permanganate is 0.001712.

Haff and Schwartz³ report satisfactory results from the use of the cobaltinitrite method in the determination of potash in treater dust from cement plants. In determining total potash the J. Lawrence Smith method is followed until the fused mass has been extracted with water. The filtrate is then treated with an excess of acetic acid (5-10 cc.) and evaporated on a steam bath to remove this acid. The residue is taken up with a little hot water, 10-15 cc. of the cobaltinitrite solution is added, and the liquid is evaporated on a steam bath to pasty consistency; it is then removed from the bath, and when the precipitate has cooled it is taken up with about 30 cc. of cold water, the precipitate being broken up thoroughly. The solution is filtered through an asbestos padded Gooch crucible and the precipitate is washed once with cold water. The remainder of the process is completed substantially in the manner prescribed by Drushel, except that sulfuric acid (1 + 1) is used instead of (1 + 7) strength after the first addition of standard permanganate. The authors also call attention to the difficulty of preserving the cobaltinitrite solution unchanged and advise against the use of a solution more than 2 weeks old.

¹ *J. Ind. Eng. Chem.*, **2**, 379 (1910).

² U. S. Dept. Agr. Bur. Chem. Bull., **152**, p. 28.

³ *J. Ind. Eng. Chem.*, **9**, 785 (1917).

It should be noted that a number of years before Shedd¹ had recommended a similar adaptation of the J. Lawrence Smith method for the determination of potash in soils. In a later article Shedd² also recommended that the solution be evaporated to a small volume before addition of the cobalt reagent and that the evaporation on the water bath be not unduly protracted. The same procedure is employed by these authors for water-soluble potash as is used in the treatment of the water extract from the J. Lawrence Smith method.

Clerfeyt³ likewise advised the use of two separate solutions for the determination of potassium by the cobaltinitrite methods, one of cobaltous nitrate in dilute acetic acid and the other an aqueous solution of sodium nitrite. The two solutions are kept separately, and the first solution is added to the second 24 hours in advance of the determination. An excess of the reagent is added gradually, with mechanical stirring, to a strong solution of the potassium salt, slightly acidified with acetic acid. The stirring is continued for 30 minutes. The beaker is then allowed to stand overnight, after which the contents are filtered on a tared filter; the precipitate is washed with 10 per cent acetic acid and then with 95 per cent alcohol and dried at 120° C. (The dried precipitate has the formula $K_2NaCo(NO_2)_6H_2O$.)

Clerfeyt claims that numerous determinations gave results within 0.1-0.2 per cent of the results obtained by the platinum method.

Strecker and Jungck⁴ state that the cobaltinitrite method is not dependable owing to the variable composition of the precipitate, but that all the potassium can be precipitated by this method and then accurately determined by the perchlorate process. They claim that potassium perchlorate can be readily reduced by titanous sulfate and by fusion with potassium nitrate and sodium hydroxide or by hydrazine sulfate and sodium hydroxide. The resulting potassium chloride solution is titrated with silver nitrate.

L. LeBoucher⁵ states that the cobaltinitrite reagent should be added dropwise, with prolonged stirring, and the precipitate allowed to stand overnight before filtering. LeBoucher claims that the method is accurate when the ratio of sodium to potassium in the solution does not exceed 15 to 1.

¹ *J. Ind. Eng. Chem.*, **1**, 302 (1909).

² *Ibid.*, **2**, 379 (1910).

³ *Bull. soc. chim. Belg.*, **31**, 417 (1922); *J. Chem. Soc.*, **124**, pt. 2, 181 (1923).

⁴ *Z. anal. Chem.*, **63**, 161 (1923); *C. A.*, **18**, 642.

⁵ *Anales. soc. espan. fis. quim.*, **23**, 540 (1925); *C. A.*, **20**, 1366.

Hamid¹ investigated the composition of the precipitate obtained in the cobaltinitrite method for the determination of potassium and found it to be the monohydrated di-potassium sodium cobaltinitrite ($K_2NaCo(NO_2)_6 \cdot H_2O$). He reports satisfactory results by this method when compared with the perchlorate method and commends it especially for use in determining potassium in the presence of sulfates. Satisfactory determinations of potassium are reported both by the gravimetric and volumetric processes.

Wenger and Hemen² proposed that instead of weighing the cobaltinitrite precipitate or titrating it with permanganate, the precipitate be treated with sulfuric or hydrochloric acid and the resulting solution electrolyzed to deposit cobalt, which is then weighed.

Bulli and Fernandes³ propose the determination of potassium by precipitating it as the triple nitrite of potassium, lead and cobalt ($K_2Pb[Co(NO_2)_6]$), the nitrite residue being titrated with permanganate. The procedure follows:

Evaporate the solution to a small volume and when cold add a large excess of sodium nitrite and lead nitrate, either in a saturated solution or as a solid, and a few crystals of cobaltous nitrate or cobaltous chloride. Allow liquid to stand for several hours with occasional shaking. Filter into a Gooch crucible, wash with water, digest for 30 minutes with an excess of 0.1 *N* potassium permanganate containing a few drops of dilute sulfuric acid, heat slowly to boiling, and add more dilute sulfuric acid. Titrate the hot solution with 0.1 *N* sodium oxalate solution. The solution to be analyzed should not contain heavy metals or ammonium salts.

Tovarnitzkii and Sergeenko⁴ state that potassium can be determined by the following procedure without the elimination of bases other than ammonium and with a maximum error of 1-2 per cent.

To 50 cc. of the solution to be tested and containing 10-20 mg. of potassium, add 2-4 cc. of $Na_2PbCo(NO_2)_6$ reagent. Stir for 20 minutes to get complete precipitation. Add barium sulfate until the precipitate changes from orange to a light yellow color. Filter through filter paper and wash with 200-250 cc. of water. Wash the precipitate from the filter into the first beaker, then add 50 cc. of 0.1 *N* potassium permanganate and 20 cc. of (1 + 3) sulfuric acid and make up to 300-400 cc. Heat the beaker on a water bath at 100° for 30 minutes. After heating, add to the beaker an excess of 0.1 *N* sodium oxalate and titrate back with 0.1 *N* potassium permanganate. Calculate the results by the formula; $x = [(a + c) - b] \times 0.0006521$, where *a* = cc. of potassium permanganate used for oxidation; *b* = cc. of sodium oxalate; *c* = cc. of permanganate used for titration and 0.0006521 is the factor.

¹ *Analyst*, **51**, 450 (1926).

² *Ann. chim. anal. chim. appl.*, **2**, 198 (1920); *C. A.*, **14**, 3382.

³ *Ann. chim. applicata*, **13**, 46 (1923); *C. A.*, **17**, 3655.

⁴ *Zhurnal Sakharnoi Promyshlennosti*, **2**, 228 (1928); *C. A.*, **23**, 1906.

The reagents required are 0.1 *N* potassium permanganate, 0.1 *N* sodium oxalate, sulfuric acid (1 + 3) and barium sulfate suspended in water. Prepare the special cobalt reagent as follows: Crush and mix 22 grams of sodium nitrite, 3 grams of cobaltous nitrate and 5 grams of lead nitrate; dissolve in a little hot water; wash into a graduate cylinder; make up to 80 cc.; and add 5 cc. of acetic acid. When the precipitation is complete, filter the solution and store the clear filtrate in dark bottles.

REDUCED CHLOROPLATINATE METHODS

In the volumetric determination of potash by the titration of the chlorine from the reduced chloroplatinate, Mohr¹ proposes to reduce the dry salt by heating with sodium oxalate, followed by extraction with hot water. The filtrate is titrated with silver nitrate solution, a soluble chromate being used as an indicator. De Koninck,² Fabre³ and Diamant⁴ suggest the reduction of a solution of the chloroplatinate by means of magnesium powder. The double salt is dissolved in boiling water, filtered, and titrated with silver nitrate.

MISCELLANEOUS METHODS

DETERMINATION OF POTASSIUM AS POTASSIUM 6-CHLORO-5-NITRO-*m*-TOLUENE SULFONATE

H. Davies and W. Davies⁵ report that potassium 6-chloro-5-nitro-*m*-toluene sulfonate is less soluble at the ordinary temperature than most of the ordinary potassium salts used for the detection of potassium, and that in the absence of ammonium the sodium salt is a cheap and useful reagent for potassium, one part of the latter in 2500 parts of water being detectable. The reagent is said to give satisfactory results in the presence of sodium or aluminum and presumably of magnesium and sulfate.

PICRATE METHOD

St. Minovici and Ionescu⁶ proposed the following method for the estimation of potash as the picrate:

To 10 cc. of a solution containing 1 gram of potash salt, add 20 cc. of a saturated solution of picric acid in 95 per cent alcohol to which 5 per cent of glycerol has been added and allow to stand 5 minutes with frequent stirring. Filter through

¹ *Z. anal. Chem.*, **12**, 137 (1873); **38**, 182 (1899).

² *Rev. Univ. mincs*, **9**, 2; No. 2 (1881); U. S. Dept. Agr. Div. Chem. Bull. **7** (1885).

³ *Compt. rend.*, **122**, 1331 (1896); *Z. anal. Chem.*, **38**, 182 (1899).

⁴ *Chem. Ztg.*, **22**, 99 (1898); *Z. anal. Chem.*, **38**, 182 (1899).

⁵ *J. Chem. Soc. Trans.*, **123**, 2976 (1923).

⁶ *Bull. soc. chim. Roumanie*, **3**, 25 (1921); *C. A.*, **15**, 3045.

a double tared filter. Wash the precipitate with 20 cc. of ether to dissolve any picric acid and dry 24 hours in a desiccator containing calcium chloride. The procedure is unaffected by the presence of 1 per cent or less of sodium or ammonia. Instead of weighing the precipitate the potassium may be determined volumetrically by titrating with a standard solution of quinine acid sulfate.

Reference may also be made to Reichard's proposal of sodium picrate as a qualitative reagent for potassium.¹

POTENTIOMETRIC METHODS

Rauch² proposed the determination of potassium by electrometric titration. The potassium, in a neutral or weakly alkaline 30 per cent by volume alcoholic solution, is precipitated by calcium ferrocyanide as potassium calcium ferrocyanide. The excess calcium ferrocyanide is determined potentiometrically by the addition of zinc sulfate in an aliquot part of the filtrate. The calcium ferrocyanide solution is standardized under the same conditions as obtain in the potassium determination. The author claims that the method is satisfactory when the quantity of potassium present does not exceed 0.1 gram and reports a number of results in support of his claim. The method can be carried out in the presence of sodium, calcium, magnesium, sulfate and chlorine ions, but the absence of ammonium, barium, nitrate, or any ions capable of forming an insoluble ferrocyanide must be assured.

A titrimetric method for the determination of potassium was proposed by G. Jander and O. Pfundt.³ It is dependent upon the determination of the saturation point by the conductometric method; a cold concentrated solution of potassium salt is used, and titration is made with a concentrated solution of sodium perchlorate.

CENTRIFUGAL METHODS

Hamburger⁴ proposed a method for applying the cobaltinitrite method to the determination of small quantities of potassium by a centrifugal process. A small volume of solution containing the potassium salt is treated with cobaltinitrite solution and allowed to stand 16 hours at 37° C. The precipitate is then centrifuged. Phosphoric acid should be removed before the potassium is precipitated.

¹ *Z. anal. Chem.*, **40**, 377 (1901).

² *Z. anorg. allgem. Chem.*, **160**, 77 (1927).

³ *Z. anal. Chem.*, **71**, 417 (1927); *C. A.*, **21**, 3852.

⁴ *Biochem. Zeit.*, **71**, 415 (1915); *J. Chem. Soc.*, **110**, pt. 2, 50 (1916).

Sherrill¹ describes a centrifugal method for the determination of potash, which he claims is both accurate and rapid, and gives results of a number of check determinations compared with results obtained by a well-known public analyst. He uses a stock cobaltinitrite solution prepared by dissolving separately 450 grams of sodium nitrite and 250 grams of C. P. cobalt acetate in 800 cc. of water, mixing the two solutions, and making up to 2 liters. This solution keeps well. The solution used as a precipitating agent is made by adding 65 cc. of water and 5 cc. of glacial acetic acid to 100 cc. of the stock solution, mixing, and letting stand overnight before using. This solution should be freshly prepared every 3-4 days. The procedure is as follows:

Transfer 5 cc. of an approximately 1 per cent potassium oxide solution of the sample to a potash centrifuge tube containing 17 cc. of the sodium cobaltinitrite solution. To a similar tube add 5 cc. of a standard 1 per cent potash solution (15.83 grams of pure potassium chloride and 8-10 drops of glacial acetic acid made up to a liter). These tubes are similar to those used in the centrifugal method for determining phosphoric acid, p. 185. Centrifuge both at once in a Babcock hand milk-test centrifuge at 1000 r.p.m. for 1 minute. Observe each tube, tap gently with the finger to level the surface of the precipitate, and centrifuge again for 15 seconds. Calculate results by the formula:

$$\frac{\text{cc. to which sample is diluted} \times \text{reading of sample}}{\text{gram of sample in above solution} \times \text{reading of standard}} = \text{percentage of K}_2\text{O}.$$

Before making up the solution of the sample to the mark, render it alkaline with 10*N* sodium hydroxide and acidify with glacial acetic acid, using phenolphthalein as an indicator. If it contains insoluble matter, filter through a dry paper and centrifuge 5 cc. of the clear filtrate. If necessary, ignite the sample to drive off ammonium salts. The stem of the tube should be full of water before adding the cobaltinitrite solution. A 4-tube head centrifuge allows three samples to be run with the one standard.

POLARIMETRIC METHOD

Wrobel² observed that when a solution containing sodium hydrogen tartrate and ammonium molybdate is treated with a potassium salt, the reaction of the latter with the tartrate results in the depression of the optical rotation of the liquid, the extent of this depression serving as a means of determining the quantity of potassium used.

¹ *J. Ind. Eng. Chem.*, **13**, 227 (1921).

² *Roczniki Chem.*, **4**, 287 (1924); *C. A.*, **19**, 2463.

DETERMINATION OF INSOLUBLE POTASH

As previously stated, in fertilizer practice only the water-soluble potash is considered. Silicates containing insoluble potash, however, are sometimes used as a source of potash. The use of greensand as a fertilizer has already been mentioned (see p. 358). The determination of insoluble potash in silicates or other rocks is most frequently made by the method of J. Lawrence Smith.¹ This method is fully described in Volume I of this publication and in *Methods of Analysis, A. O. A. C.*, in the section on soils.

OFFICIAL METHODS

In many countries official methods for analyzing fertilizer materials are included in statutory regulations; in others they are specified by trade, agricultural or scientific associations for use in the work of such societies. In this section the official methods of only three foreign countries are given in detail since those of other countries are similar to these three or to those of the United States.

UNITED STATES

Two modifications of the platinum method are official in the United States. Complete descriptions of these are found in *Methods of Analysis, A. O. A. C.*

SPAIN²**(a) PERCHLORATE METHOD (SCHLOESING AND SERULLAS)**

Muriate.—Dissolve 50 grams of the material in water, dilute the solution to 1 liter and mix thoroughly. To 20 cc. of this solution, corresponding to 1 gram of the substance, add dropwise a solution of barium nitrate until it no longer produces turbidity. (This condition can be easily noted by causing drops of the reagent to flow down the sides of the vessel containing the solution.) Transfer the liquid without filtering to a small evaporating dish, washing twice with very little water, and concentrate on a sand bath until the volume is approximately 5 cc. Add 5 cc. of nitric acid two or three times in succession, evaporating each time to a small bulk, without raising the temperature too high. The chlorine is thus eliminated, but in order to be sure of this elimination, the vapors are condensed on a glass plate and are then treated with silver nitrate, which should not produce a precipi-

¹ *Am. J. Sci.*, [3] **1**, 269 (1871); *Am. Chemist*, **1** (1871); *Ann. Chem. und Pharm.*, **159**, 82 (1871).

² Procedimientos de Análisis de Abonos, formulated by the director of the Agronomy Station of the Agricultural Institute of Alfonso XII and required in the agricultural laboratories of the Department of Public Works. Madrid, 1919.

tate. Add 10 cc. of perchloric acid solution containing 1.6 grams of the actual acid in 10 cc. of solution. (Take 100 grams of perchloric acid of a density of 1.7, which contains 90 per cent pure perchloric acid, and dilute to 550 cc. with distilled water.)

Evaporate to dryness on a sand bath; the operation is complete when the white fumes due to excess of perchloric acid are no longer produced. Then add 5 or 6 drops of water and evaporate to dryness. After the dish is cool add 10 cc. of 95 per cent alcohol which has previously been saturated with pure potassium perchlorate. Crush the crystalline mass with a rod so that the alcohol can impregnate it well; allow it to stand and decant the alcohol, washing through a small Berzelius or Schleicher and Schull filter paper. Add 5 cc. of alcohol to the dish and proceed in the same manner as before, repeating the operation three or four times. After decanting for the last time, add 5 cc. of water to the residue, heat to dryness over a sand bath and treat the residue for the last time with a few cubic centimeters of alcohol, which is also decanted through the filter.

In the dish and on the filter there will be left after this treatment only a mixture of potassium perchlorate with a very small quantity of insoluble barium sulfate. In all these washings do not use more than from 40 to 50 cc. of the alcohol saturated with potassium perchlorate. Add to the dish 20 cc. of water and heat to boiling on a sand bath, avoiding spattering. Pour the hot liquid in which the potassium perchlorate has been dissolved through the same filter as was used before and through which the alcohol washings were decanted.

Receive the perchlorate solution in a small porcelain evaporating dish previously tared. Add 5 cc. more of water to the first dish, boil it, and pass it through the filter. Repeat this washing with boiling water four or five times more, using each time 5 cc. of water. As these liquids are received in the tared dish, they are evaporated so that the dish may hold all the wash waters.

In order to keep the potassium perchlorate from creeping over the sides of the dish, add, before beginning the operation, 2 or 3 drops of perchloric acid.

When the evaporation is completed and the white fumes, due to excess of perchloric acid, have disappeared, raise the temperature to 150° for about 10 minutes and then allow the dish to cool in a desiccator over sulfuric acid and weigh. The increase in weight is due to the potassium perchlorate.

On multiplying by 33.9, the potassium contained in 100 grams of the salt analyzed will be found.

Sulfate of potash or a mixture of salts containing large quantities of sulfates.—Dissolve 25 grams of sulfate, or of the salt to be analyzed in a 500 cc. flask with 100 cc. of boiling water, agitating during the process of solution; decant into a 500 cc. volumetric flask and wash out the original flask several times with very small quantities of boiling water, bringing the volume to 500 cc. with these washings after cooling.

Shake well to obtain a homogeneous liquid and heat 20 cc. of the solution, corresponding to 1 gram of the substance, to boiling in a 200 cc. flask and add barium nitrate until a further addition does not give a precipitate. Add a slight excess of powdered ammonium carbonate, which precipitates the excess of barium, boil a few minutes and filter. Evaporate the liquid to a small volume on a sand bath; add 10 cc. of aqua regia, containing one fifth part of hydrochloric acid; continue the evaporation to dryness, placing an inverted funnel over the dish; and

add aqua regia once or twice more, eliminating it by evaporation, by which means the salts of ammonium are destroyed. Take up the residue with nitric acid, evaporate to dryness, and add 10 cc. of perchloric acid in the same manner as in the treatment of a chloride.

Evaporate again until white fumes of perchloric acid are driven off, and wash as in the case above, with 95 per cent alcohol saturated with potassium perchlorate. Since in this case there is no insoluble residue other than the perchlorate, it is sufficient to dissolve, after the washing, with a very small quantity of boiling water, which is passed through the filter, receiving the liquids in a small weighed porcelain dish; evaporate to dryness, cool, weigh, and multiply by 33.90 to obtain the percentage of potash in the material.

Complete fertilizer containing organic nitrogen, salts of ammonia, superphosphate, and potash in the form of chloride or sulfate.—Mix intimately, in a mortar, 5 grams of the substance with one gram of hydrated lime. Transfer to a porcelain dish and moisten the mass with a few drops of water. Desiccate and calcine slowly, at a low temperature (not exceeding a dark red). Take up the residue with a small quantity of boiling water, filter, and wash with boiling water in such amount that the whole volume of collected liquid in which the potash is dissolved is about 80 cc. Add to this liquid a slight excess of baryta water. Separate the excess barium by adding a concentrated ammonium carbonate solution, avoiding too great an excess. Boil, filter, wash, evaporate to a small volume, and treat several times with aqua regia containing $\frac{1}{5}$ hydrochloric acid, evaporating each time, and finally complete the process as in the preceding analysis of sulfate of potash. Multiply the final weight by 0.339 and by 20 (since 5 grams of the substance was used), thus obtaining the percentage of potash. When the fertilizer to be analyzed is very rich in potash, use 2 grams instead of 5 grams as directed above.

(b) REDUCED PLATINUM METHOD (CORENWINDER AND CONTAMINE)

The reduced platinum method is applicable to potash salts and to mixed fertilizers if they do not contain ammonia. If ammonia is present, it is necessary to heat the substance first to a red heat to eliminate the ammonium salts, taking care however not to raise the temperature too high, nor to heat too long, as this would volatilize the potassium salts.

Dissolve 25 grams of the material, which has been previously calcined or not, depending on the presence or absence of ammonium salts, in boiling water; cool; make up to a liter and mix. Filter and acidify 20 cc. of the filtrate, equivalent to 0.5 gram of the material, with hydrochloric acid. Evaporate to dryness in a tared porcelain evaporating dish and weigh the residue in order to be able to calculate the amount of chloroplatinic acid solution required; 1 cc. of solution is required for each decigram of residue. Use a chloroplatinic acid solution containing 17 grams of platinum in 100 cc.

Evaporate the mixture to a sirupy consistency on a water bath, placing a disk of cardboard between the dish and the metal ring of the bath to prevent the temper-

ature from rising above 100°. Avoid complete desiccation. Cool, add 15 cc. of 95 per cent alcohol, and digest for at least 6 hours under an inverted bell jar. After 6 hours or more stir several times with a rod, decant the supernatant liquid onto a small filter, and wash the residue with alcohol until the washings are completely colorless. Decant all the wash liquid onto the filter. Treat the material remaining in the dish with boiling water, pouring the liquid upon the same filter, until all the chloroplatinate is dissolved; repeat the operation until the liquid which passes through, as well as the filter itself, is completely colorless. Receive the chloroplatinate solution in a Bohemian glass dish, heat to boiling on a sand bath, and add a 10 per cent solution of sodium formate in successive small portions; remove the dish from the heat if the reaction is very strong but replace it before adding the next portion. Continue adding the sodium formate until the solution is completely decolorized, precipitating the platinum in the metallic state as a fine black powder.

Instead of adding the sodium formate to the chloroplatinate solution, the latter may be filtered directly into 50 cc. of boiling formate solution in a Bohemian glass dish, care being taken to avoid spattering.

Evaporate the liquid to about one-half its volume, in order to coagulate the precipitate; pour onto a small filter, and transfer the platinum which has collected in the bottom of the dish to the same filter by means of cold 10 per cent hydrochloric acid solution. When all the platinum is on the filter, complete the washing with boiling water. If any platinum passes through the filter (which is recognizable by a gray metallic tint imparted to the filtrate), let the filtrate stand until the following day and after decanting the clear supernatant liquid transfer to the filter the small deposit that may have formed, using for this purpose the necessary amount of cold water.

Dry the filter, calcine at red heat, weigh, and deduct the filter paper ash, thereby obtaining the amount of platinum equivalent to the potash contained in 5 grams of the material analyzed. Multiply this weight by 0.477 and by 200 to obtain the percentage of potash.

(c) THE PLATINUM METHOD (CLASSICAL PROCEDURE)

Potash Salts.—Weigh 5 grams of the substance and place in a flat-bottomed 500 cc. volumetric flask. Add 125 to 150 cc. of water and boil. While boiling, add dropwise, a solution of barium chloride (by proceeding with care it is possible to avoid more than a slight excess). Since, in general, the quantity of barium sulfate precipitate is small, it is rarely necessary to filter except when dealing with potassium sulfate.

Allow the solution to cool and dilute to 500 cc. When completely clear, evaporate 50 cc. (equivalent to $\frac{1}{2}$ gram of the substance), in a porcelain evaporating dish with a concentrated chloroplatinic acid solution (17 grams of platinum in 100 cc.). Assuming that all the substance is potassium chloride 6 cc. of platinum solution will be sufficient. Evaporate to a sirupy consistency on a water bath, placing the dish on an asbestos cardboard disk, which should overlap the metallic ring of the bath.

Add 95 per cent alcohol and let stand under a bell jar for several hours. Then decant the liquid onto two filter papers of equal weight placed one inside the other.

Wash the precipitate with a mixture of equal parts of water and alcohol, passing the washing through the same filters, and continue washing until the liquid comes through clear. (It is not wise to prolong the washing since the precipitate is somewhat soluble.)

Dry the precipitate at 90°. Weigh, with the empty filter on the weight pan of the scales, and multiply the weight obtained by 0.193 and by 200 to obtain the percentage of potash.

Complete Fertilizer.—Calcine 5 grams of the substance at a red heat without unduly prolonging the operation. Treat the ash with hot water; shake well and digest for a time. Filter and wash, collecting all the resulting liquids.

Add a small excess of baryta water to the filtrate (to make certain treat a small portion of the clear liquid, in a test tube, with baryta water to see that it produces no precipitate). Filter and wash, collecting all liquids. Add an excess of ammonium carbonate solution (proceeding as before to make sure of an excess of this reagent). Boil, filter and wash. Evaporate to dryness in a platinum dish. Cover the dry product in the dish with 4 or 5 grams of powdered oxalic acid and moisten the whole with a few drops of water. Cover with a funnel, and heat again on a sand bath, adding a few drops of water at intervals to avoid the formation of a crust.

Continue to heat at a higher temperature until all gases are driven off and finally bring the dish for an instant to a red heat. Treat the residue with a small quantity of hot water, shake well, and rub off the particles which may adhere to the dish. Repeat this operation, with small quantities of hot water collecting all the material on a small filter. Wash the filter, using the same precautions, and collect all the liquids in a small, exactly tared, porcelain dish. Add hydrochloric acid dropwise to the filtered solution until it gives an acid reaction. Evaporate to dryness, allow to cool, and weigh the mixture of chlorides thus obtained. Treat the mixture with just sufficient water to dissolve the salts. Add a concentrated solution of chloroplatinic acid. (One cc. of platinum solution suffices for 0.1 gram of the mixture of chlorides.)

Evaporate to a sirupy consistency on a water bath, using a cardboard disk as before. Add 95 per cent alcohol and proceed as under potash salts.

Multiply the weight obtained by 0.193 and by 20 to obtain the percentage of potash in the fertilizer.

GERMANY¹

Potassium is determined by the platinum or perchlorate method, but the latter is more generally used. It has the advantage over the platinum method in that it permits an easier handling of sulfates. The perchlorates of sodium, calcium, magnesium and barium are soluble in alcohol so that the use of a small excess of barium chloride for precipitating the sulfuric acid of the sulfates does no harm. In the platinum method, however, even a small excess of barium chloride is to be avoided. The sulfuric acid of

¹ Methoden zur Untersuchung der Kunstdüngemittel. Verein Deutscher Dünger Fabrikanten, Braunschweig, 1925.

the sulfates is precipitated from the boiling salt solution by the dropwise addition of barium chloride from a buret. The end of the precipitation can be told very accurately by the addition of a small crystal of barium chloride to the solution that has become clear by settling, giving no turbidity. In the platinum method any slight excess of barium chloride should be eliminated in every case by the addition of a few drops of dilute sulfuric acid.

PLATINUM METHOD

REAGENTS

1. *Chloroplatinic acid*.—10 cc. of solution, sp. gr. 1.18, should contain 1 gram of platinum. Make certain that the solution contains neither platinous chloride nor oxidized nitrogen compounds.

2. *Barium chloride*.—Dissolve 122 grams of crystalline barium chloride in water to which has been added 50 cc. of concentrated hydrochloric acid made up to 1 liter with water.

3. *Alcohol*.—For washing the potassium chloroplatinate use alcohol that is at least 96 per cent by weight.

DETERMINATION

Evaporate in a shallow porcelain dish of about 10 cm. diameter, on a water bath, with frequent swirling, an aliquot portion of the salt solution or of the filtrate from the barium sulfate precipitation with 6 cc. of chloroplatinic acid solution. The evaporation can be carried to dryness without danger since in addition to the potassium chloroplatinate the corresponding sodium compound is chiefly present and it is more readily dissolved by alcohol in the absence of water than in its presence. Rub the dry residue from the evaporation carefully with a glass pestle, and stir thoroughly with 20–25 cc. of alcohol of at least 96 per cent by weight. Pour the washings through a filter paper that has been moistened with alcohol, dried to constant weight at 120°–130°,—for which an hour is usually sufficient—and weighed warm, taking care that the liquid does not touch the rim of the paper; repeat the stirring with alcohol several times, pouring each time upon the filter paper, and transfer the precipitate to the filter. The filtration can be hastened by the use of moderate suction. A very rapid washing of the potassium chloroplatinate can be made by the use of hot alcohol. Free the filter paper and the precipitate from alcohol as completely as possible by suction and by pressing between filter paper and dry to constant weight at 120°–130°, 20 minutes is usually sufficient time, and weigh warm. The use of the Gooch crucible has unmistakable advantage over the filter paper.

PERCHLORATE METHOD

REAGENTS

1. *Perchloric acid*.—Sp. gr. 1.125 = 20 per cent HClO_4 . It must be free from sulfuric acid. No turbidity should appear on the addition of either barium chloride or alcohol.

2. *Barium chloride*.—As described above.
3. *Alcohol*.—Alcohol that is 96 per cent by weight and alcohol containing 0.2 per cent of HClO_4 . Add 10 cc. of perchloric acid, sp. gr. 1.125 to a liter of alcohol.

DETERMINATION

Evaporate with perchloric acid in a shallow, dark blue, glazed porcelain dish of about 10 cm. diameter on a water bath an aliquot portion of the salt solution or of the filtrate from the barium sulfate precipitation until the odor of hydrochloric acid disappears and white fumes of perchloric acid are evolved. Allow to cool, cover the residue from the evaporation with 20 cc. of 96 per cent alcohol, and triturate thoroughly. Allow to stand a short time and filter the liquid standing over the potassium perchlorate through a filter or a Gooch crucible. Repeat the trituration of the potassium perchlorate twice more, not with pure alcohol but with alcohol to which has been added 0.2 per cent of perchloric acid. Wash the residue onto a filter paper or into a crucible and wash with perchloric acid alcohol. Finally, in order to free the filter and precipitate from perchloric acid, wash with a small amount of pure alcohol. Dry the filter and precipitate to constant weight at 120° – 130° , for which 20 minutes is usually sufficient, and weigh.

PRÉPARATION OF THE SOLUTION

Take a large sample, at least 0.5 kg., and grind it in a mill or mortar until it completely passes a 1 mm. sieve; never reject pieces that are difficult to reduce. In order to avoid calculation of the percentage content from the weight of the precipitate in each analysis, weigh out such an amount of the salt to be analyzed that its weight in grams is a multiple of the gravimetric factor. The factors of the platinum method have been experimentally determined. It makes no difference whether the potash salts are dissolved in pure water or in water containing hydrochloric acid, but since hydrochloric acid must be added to the solution before precipitating the sulfuric acid, the acid may as well be added at the time the salts are dissolved.

A. Crude Potash Salts

CARNALLITE, KAINITE, SYLVINITE, HARTSALZ, BERGKIESERITE

Platinum method.—(a) Dissolve 9.655 grams of the sample in a 500 cc. flask with 300 cc. of boiling water to which has been added 20 cc. of concentrated hydrochloric acid. Add barium chloride (see above), cool, make up to 500 cc., and filter. Evaporate 10 cc. of the filtrate ($= 0.1931$ gram) with 4 cc. of chloroplatinic acid solution. 1 mg. $\text{K}_2\text{PtCl}_6 = 0.1$ per cent K_2O .

(b) Dissolve 7.640 grams of the sample in a 500 cc. flask, etc. Use 20 cc. of the filtrate ($= 0.3056$ gram) with 6 cc. of chloroplatinic acid solution. 1 mg. $\text{K}_2\text{PtCl}_6 = 0.1$ per cent KCl .

Perchlorate method.—(a) Dissolve 8.488 grams of the sample in a 500 cc. flask with 300 cc. of boiling water to which has been added 20 cc. of concentrated

hydrochloric acid. Precipitate the sulfuric acid and make up to 500 cc. Evaporate 20 cc. of the filtrate (= 0.3399 gram) with 5 cc. of perchloric acid. 1 mg. KClO_4 = 0.1 per cent K_2O .

(b) Dissolve 13.4525 grams of sample as under (a). Evaporate 20 cc. of the filtrate (= 0.5381 gram) with 8 cc. of perchloric acid. 1 mg. KClO_4 = 0.1 per cent KCl.

B. Concentrated Potash Salts

1. MURIATE

Platinum method.—Dissolve 7.640 grams of the sample, make up to 500 cc., etc. Evaporate 20 cc. of the filtrate with 6 cc. of chloroplatinic acid. 1 mg. K_2PtCl_6 = 0.1 per cent KCl.

Perchlorate method.—Dissolve 13.4525 grams, make up to 500 cc., etc. Evaporate 20 cc. with 8 cc. of perchloric acid. 1 mg. KClO_4 = 0.1 per cent KCl.

2. SULFATE OF POTASH AND SULFATE OF POTASH AND MAGNESIA

Make the sulfate precipitation in a solution strongly acid with hydrochloric acid, in order to prevent, so far as possible, the carrying down of the potash by the barium sulfate.

Platinum method.—Dissolve 8.9275 grams of the sample in a 500 cc. flask with 300 cc. of boiling water, to which has been added 20 cc. of concentrated hydrochloric acid. Precipitate the sulfuric acid as described above. Evaporate 20 cc. of the filtrate (= 0.3571 gram) with 6 cc. of chloroplatinic acid solution. 1 mg. K_2PtCl_6 = 0.1 per cent K_2SO_4 . Add 0.3 per cent to the potassium sulfate content found in the sulfate of potash. No correction is necessary with the sulfate of potash and magnesia.

Perchlorate method.—Dissolve 15.7218 grams of the sample in a liter flask with 700 cc. of boiling water to which 30 cc. of hydrochloric acid has been added. Precipitate the sulfuric acid and make up to a liter. Evaporate 40 cc. of the filtrate (= 0.6289 gram) with 8 cc. of perchloric acid. 1 mg. KClO_4 = 0.1 per cent K_2SO_4 . In the case of sulfate of potash, add 0.3 per cent of potassium sulfate to the determined content.

C. Potash Salts

Express content of the potash fertilizer salts in per cent K_2O or KCl; make the analysis as for the crude potash salts.

D. Mixed Fertilizers

POTASH-SUPERPHOSPHATE AND POTASH-AMMONIUM SUPERPHOSPHATE MIXTURES

Extract 20 grams of the substance twice by boiling with two 150 cc. portions of water. Transfer the solution to a liter flask and make up to the mark. Precipitate 200 cc of the filtrate at boiling temperature in a 400 cc. flask, with barium

chloride. Treat with baryta water until an alkaline reaction is obtained, cool, and make up to 400 cc.; mix by shaking and treat 200 cc. of the boiling filtrate with ammonium carbonate. Make up again to 400 cc. and filter. Evaporate 200 cc. (= 1 gram of the substance) in a platinum dish, dry at 130°–150° and volatilize the ammonium salts by gentle ignition. Take up the residue with hot water, filter, and wash. Acidify the filtrate faintly with hydrochloric acid and evaporate with chloroplatinic acid, or with perchloric acid.

ORGANIC MIXTURES

Ash 10 grams of the substance in a platinum dish and boil the residue with 50 cc. of concentrated hydrochloric acid and a few drops of nitric acid in a 500 cc. flask for 30 minutes; cool, dilute, and precipitate with barium chloride. Make up to the mark and filter. Neutralize 50 cc. of the filtrate with ammonia and add ammonium carbonate. Bring to a boil, filter, and wash. Transfer the solution to a platinum dish, evaporate, remove the ammonia salts by gentle ignition, etc.

For mixed fertilizers composed of many constituents, the following method of Finkener and Neubauer¹ is also recommended. In this method the precipitation of sulfuric acid with barium chloride is omitted and metallic platinum is weighed.

Large quantities of organic matter are previously destroyed by careful ashing or by oxidation with nitric acid and sulfuric acid according to the method of Neumann.

Boil 10 grams of the substance (or treat as above if necessary) for ½ hour in a 500 cc. volumetric flask with 300 cc. of water. Add a few drops of phenolphthalein and treat with dilute pure milk of lime until a distinct red color appears. Continue to boil for a time in order to drive off the ammonia as completely as possible and thus render the phosphoric acid precipitation more complete. Cool, make up to the mark, mix the solution, and filter. Acidify 25 or 50 cc. of the filtrate faintly with hydrochloric acid and evaporate in a platinum dish. If nitrates are present, evaporate previously three times with a little hydrochloric acid in a glass or porcelain dish and then transfer to the platinum dish. Heat the residue in the platinum dish over a mushroom top burner, cautiously at first and then strongly enough to drive off the ammonia salts. Digest the residue with very dilute hydrochloric acid, evaporate again if necessary, to get rid of silicic acid, filter into a porcelain dish, and wash. Add chloroplatinic acid and evaporate. Allow the resulting mass of salts to cool, moisten with 0.5 cc. of water and triturate with a glass rod. Add 35 cc. of alcohol in three equal portions and triturate thoroughly each time. Allow to stand one-half hour and filter through a Neubauer platinum sponge crucible and wash with alcohol. Dry the crucible, place over it a pierced porcelain cover equipped with an inlet tube and reduce the platinum salts by the introduction of illuminating gas. In doing this, first heat the crucible with a tiny flame and then increase the heat until the crucible is barely red. Heat 20 minutes,

¹ *Z. Anal. Chem.*, **39**, 481 (1900); **46**, 311 (1907); *Landw. Vers. Sta.*, **57**, 461 (1902).

turn off the gas, allow the crucible to cool, and moisten its contents thoroughly with cold water. Draw hot water through 15 times in order to remove the easily soluble salts. To remove the difficultly soluble salts (gypsum), submerge the crucible to one-half its depth for one-half hour in hot 15-20 per cent nitric acid. Suck free of acid and wash thoroughly with hot water. Dry the crucible, ignite thoroughly, cool, and weigh. The experimentally determined factor for platinum to potassium oxide is 0.48083.

GREAT BRITAIN¹

Potash shall be determined by the perchloric acid method or, alternatively, by the platinum chloride method.

(1) PERCHLORIC ACID METHOD

(a) *Salts of potash free from sulfates.*—A weighed portion of the sample equivalent in potash content to 1.5-2.0 grams of potash (K_2O) shall be dissolved in water. The solution shall be filtered if necessary and made up to 500 ml. The potash shall be determined in 50 ml. of the solution by precipitation with perchloric acid, as prescribed in (1) (d).

(b) *Salts of potash containing sulfates.*—(A) A weighed portion of the sample equivalent in potash content to 1.5-2.0 grams of potash (K_2O) shall be boiled with 300 ml. of water to which 20 ml. of hydrochloric acid have been added. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulfuric acid is completely precipitated. The liquid shall be cooled, made up to 500 ml. and filtered, 50 ml. of the filtrate shall be taken and evaporated to dryness and shall then be moistened with concentrated hydrochloric acid, again evaporated to dryness, treated with a little dilute hydrochloric acid and filtered if necessary. The potash shall be determined by precipitation with perchloric acid as prescribed in (1) (d).

If the solution contains phosphates, iron, manganese or other substances that would interfere with the determination of potash, the method prescribed in (1) (c) is to be used instead of the method prescribed in (1) (b).

(B) *Alternative method.*—A weighed portion of the sample equivalent in potash content to 1.5-2.0 grams of potash (K_2O) shall be boiled with 300 ml. of water, cooled, made up to 500 ml. and filtered. To 50 ml. of the filtrate, 30 ml. of a solution of sodium cobaltinitrite shall be added, the mixture stirred and allowed to stand for not less than 2 hours. It shall then be filtered and washed with water containing a small amount of the cobaltinitrite solution. The precipitate shall be dissolved in hot dilute hydrochloric acid and the solution filtered into a small porcelain dish and evaporated to dryness. The residue shall be dissolved in water and the potash determined by precipitation with perchloric acid as prescribed in (1) (d).

(c) *Potash in guanos and mixed fertilizers.*—(A) 10 grams of the sample shall be gently incinerated in order to char organic matter, if present, and shall then be heated for 10 minutes with 10 ml. of concentrated hydrochloric acid and finally boiled with 300 ml. of water. The liquid shall be filtered and raised to the

¹ Statutory Rules and Orders No. 421, 17-21 (1928).

boiling point, and powdered barium hydroxide shall be added until slightly alkaline. It shall then be cooled, made up to 500 ml. and filtered. Of the filtrate, 250 ml. shall be treated with ammonia solution and an excess of ammonium carbonate and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 ml. and filtered. Of the filtrate, 100 ml. are to be evaporated in a porcelain dish to dryness. If desired, nitric acid may be added during the evaporation after free ammonia has been driven off. The residue is to be heated gently over a low flame till all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be moistened with concentrated hydrochloric acid, evaporated to dryness, treated with dilute hydrochloric acid, and filtered. The potash shall be determined in the filtrate by precipitation with perchloric acid as prescribed in (1) (d).

(B) *Alternative method.*—10 grams of the sample shall be gently incinerated in order to char organic matter, if present, and shall then be heated for 10 minutes with 10 ml. of concentrated hydrochloric acid and finally boiled with 300 ml. of water. The liquid shall be filtered into a half-liter flask and the residue washed. The solution shall be made up to 500 ml., and 50 ml. shall be taken, boiled with solution of sodium nitrite to expel ammonium salts, if present, and evaporated to dryness. The residue shall be dissolved in water containing a little hydrochloric acid and sufficient sodium citrate added to prevent precipitation of phosphates. It shall then be mixed with 30 ml. of cobaltinitrite solution, in the manner described in (1) (b) (B) and the precipitate treated as therein directed.

(d) *Precipitation of potash as potassium perchlorate.*—To the solution obtained as described in (1) (a), (b) or (c) and placed in a small glass or porcelain basin, about 7 ml. of a 20 per cent solution of perchloric acid (sp. gr. 1.125), free from chloric acid, shall be added. The basin shall be placed on a hot plate or sand bath and the contents evaporated until white fumes are copiously evolved.

The precipitate shall be re-dissolved in hot water, a few drops of perchloric acid solution added and the whole concentrated again to the fuming stage. After being cooled, the residue in the basin shall be thoroughly stirred with 20 ml. of alcohol of sp. gr. 0.816–0.812 (95–96 per cent of alcohol by volume). The precipitate shall be allowed to settle, and the clear liquid shall be poured through a weighed or counterpoised filter paper, or through a Gooch crucible, the precipitate being drained from the liquid as completely as possible before adding the washing solution. The precipitate shall be washed by decantation with alcohol (as above), saturated with potassium perchlorate at the temperature at which it is used, the washings being poured through the paper or Gooch crucible on which the whole of the precipitate is finally collected, dried at 100° C., and weighed. The precipitate is to be regarded as $KClO_4$ and is to be calculated to its equivalent as K_2O .

(e) *Preparation of the cobaltinitrite solution.*—The cobaltinitrite solution shall be prepared as follows: 50 grams of cobalt nitrate and 300 grams of sodium nitrite shall be dissolved in water, acidified with 25 ml. of glacial acetic acid and diluted to a liter. The solution shall be filtered after standing 24 hours, and it is then ready for use. It must be kept in the dark.

(2) PLATINUM CHLORIDE METHOD

(a) *Salts of potash free from sulfates.*—A weighed portion of the sample equivalent in potash content to 1.5–2.0 grams of potash (K_2O) shall be dissolved in water; the solution shall be filtered if necessary and made up to 500 ml. The potash shall be determined in 50 ml. of the solution by the platinum chloride method prescribed in (2) (d).

(b) *Salts of potash containing sulfates.*—A weighed portion of the sample equivalent in potash content to 1.5–2.0 grams of potash (K_2O) shall be boiled with 300 ml. of water to which 20 ml. of hydrochloric acid have been added. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulfuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulfuric acid. The liquid shall be cooled, made up to 500 ml., and filtered; 50 ml. of the filtrate shall be taken and evaporated to dryness and shall then be moistened with concentrated hydrochloric acid, again evaporated to dryness, treated with a little dilute hydrochloric acid, and filtered if necessary. The potash shall be determined in the filtrate by the platinum chloride method, prescribed in (2) (d).

If the solution contains phosphates, iron, manganese, magnesium or other substances that would interfere with the determination of potash, the method prescribed in (2) (c) is to be used instead of the method prescribed in (2) (b).

(c) *Potash in guanos and mixed fertilizers.*—10 grams of the sample shall be gently incinerated in order to char organic matter, if present, and shall then be heated for 10 minutes with 10 ml. of concentrated hydrochloric acid and finally boiled with 300 ml. of water. The liquid shall be filtered and raised to the boiling point, and powdered barium hydroxide shall be added until slightly alkaline. It shall then be cooled, made up to 500 ml. and filtered. Of the filtrate, 250 ml. shall be treated with ammonia solution and an excess of ammonium carbonate and then, while boiling, with a little powdered ammonium oxalate; cooled; made up to 500 ml.; and filtered. Of the filtrate, 100 ml. are to be evaporated in a porcelain dish to dryness. If desired, nitric acid may be added during the evaporation, after free ammonia has been driven off. The residue is to be heated gently over a low flame till all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be moistened with concentrated hydrochloric acid, evaporated to dryness, treated with dilute hydrochloric acid, and filtered. The potash shall be determined in the filtrate by the platinum chloride method prescribed in (2) (d).

(d) *Precipitation of potash as potassium chloroplatinate.*—To the solution obtained as described in (2) (a), (b) or (c), a few drops of hydrochloric acid shall be added, if none is present, and also 10 ml. or an excess of solution of platinum chloride containing 10 grams of platinum per 100 ml. After evaporation to a sirupy consistency on a water-bath, the contents of the basin shall be allowed to cool and shall then be treated with alcohol, sp. gr. 0.864, being washed by decantation until the alcohol is colorless. The washings shall be passed through a weighed or counterpoised filter paper, on which the precipitate shall be finally collected, washed with alcohol as above, dried at 100° C., and weighed. The precipitate is to be regarded as K_2PtCl_6 and is to be calculated to its equivalent as K_2O .

OTHER COUNTRIES

France.¹—Methods similar to the Spanish methods are used in France.

Austria.²—A perchlorate method similar to the German perchlorate method is used in Austria.

Sweden.³—Both the perchlorate and platinum methods are used. The former is similar to the German perchlorate method, but in the platinum method metallic platinum is weighed, reduction of the potassium chloroplatinate being accomplished with magnesium ribbon.

Norway.⁴—The perchlorate method is used in Norway.

Denmark.⁵—A platinum method similar to the alternative method of the A. O. A. C. is used.

India.⁶—The methods of India follow the official methods of the A. O. A. C. very closely.

New Zealand.⁷—A perchloric acid method like the German method is official in New Zealand.

Ireland.⁸—Potash in fertilizers is determined by a perchlorate method and by weighing potassium chloroplatinate in a manner similar to the German method.

¹ *Methodes d'Analyse des Engrais*. Ministere de l'Agriculture, Paris, 1897.

² *Methodbuch Verband der Landwirtschaftlichen Versuchstationen im Österreich*, 1st ed., Wien, 1913.

³ Kungl. Lantbruksstyrelsens Kungörelse; angående bestämmelser för undersökning vid de med statsmedel understödda kemiska stationerna. Stockholm, 1927.

⁴ *Analyse Av For-Og Gjdselstoffer*; Utarbeidet i Samarbeide Med Bestyrerne av Statens Landbrukskjemiske Kontrollstasjoner. Kristiania, 1924.

⁵ *Faelles Arbejdsmetoder for Undersgelser foretagne i Medfr of Lov om Handel med Gdnings- og Foderstoffer*, 1898.

⁶ Bulletin No. 164 of the Agricultural Research Institute, Pusa. *Standard Methods of Analysis of Fertilizers*. Calcutta, 1926.

⁷ Regulations under the Fertilizers Act, 1927. *New Zealand Gazette*, No. 74, October 4, 1928.

⁸ *The Fertilizers and Feeding Stuffs Regulations (Methods of Analysis, Ireland)*, 1918.

CHAPTER VII

MISCELLANEOUS FERTILIZERS AND SOIL AMENDMENTS

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Certain materials, which have an indirect fertilizer effect, are often added to the soil to increase its productivity. Such fertilizer materials have a beneficial effect on the growth of plants by supplying a needed plant nutrient and by producing physical and chemical changes in the soil that are favorable for increased activities of the micro-organisms.

I.—LIMING MATERIALS

Liming materials are used to neutralize acidity in the soil. Calcium is the principal constituent, but magnesium is often present. Calcium occurs fifth in the order of abundance among the 80 or more chemical elements that are components of the earth's crust. The principal forms in which calcium compounds occur are calcite, limestone, dolomite, marl, marble and gypsum; the shells of fresh water and marine mollusks; the skeletons of animals; phosphate rock, fluorspar, and silicates of calcium. Liming materials are obtained directly from some of these compounds or they are produced as by-products or as waste materials. They include caustic lime, hydrated lime, precipitated calcium carbonate, basic slag, gas lime, tannery lime, nitrolime, limekiln ashes, calcite and marble waste.

MATERIALS CONTAINING CALCIUM CARBONATE

Calcite, Calc Spar, CaCO_3 , is the purest form of calcium carbonate occurring in nature. The mineral calcite is of common occurrence in limestone rocks, and relatively pure crystalline deposits are frequently found in cracks and seams in limestone strata, also in caverns as stalactite and stalagmite deposits. Calcite is easily recognized by its colorless or clear, crystalline form, peculiar cleavage and softness and by its solubility in acids with vigorous effervescence.

The better grade of calcite has several commercial uses which make it too valuable a material to be used for liming the soil when other cheaper but less pure forms of calcium carbonate can be used as well. How-

ever calcite refuse accumulates in considerable quantity from the mining of more valuable minerals and forms a very satisfactory liming material. Calcite is also the principal mineral constituent of crystalline limestone.

Limestones.—Numerous high and medium grade deposits of readily accessible limestone rocks, which are suitable for liming material when ground to the proper fineness, occur in various parts of this country. During the past 25 years the use of ground limestone for liming acid soils in the humid portions of this country has been greatly extended. This increase in the use of limestone over burned lime, which was formerly the principal liming material used for the neutralization of acidity in soils, has resulted from a more extensive growing of leguminous crops and also from a decrease of the available supply of wood as a fuel for burning limestone to lime. It is also due to the development of better roads, and machinery for grinding and spreading ground limestone and marl. Then, too, it has been demonstrated that in most instances ground limestone is a more satisfactory and convenient liming material than is caustic lime.

Limestones vary considerably in their content of calcium carbonate. The oolitic and crystalline stones are the purest; they often contain as much as 98 per cent of calcium carbonate, as well as a small quantity of magnesium carbonate. Such high-grade limestones, however, have other industrial uses, and when favorably located with respect to transportation, they may command a price that prohibits their use as a liming material. Limestones that have a combined percentage of calcium and magnesium carbonates, *i. e.*, neutralizing power, ranging from 80 to 100 per cent, may be considered satisfactory material for agricultural use, and except for very short hauls it might not be profitable to transport material containing less than 80 per cent of calcium carbonate and magnesium carbonate.

Dolomitic Limestone.—The theoretical composition of dolomite is 54.3 per cent of calcium carbonate and 45.7 per cent of magnesium carbonate. These limestones have a flinty fracture, and their characteristic density and hardness render them more difficult to grind than limestones that contain only a small proportion of magnesium carbonate. A dolomitic limestone can be readily recognized by the comparative slowness with which it dissolves in cold, dilute hydrochloric acid. Owing to the longer time required for the solution of dolomitic limestone in dilute mineral acids, the question may be raised as to whether or not such limestone, when applied to the soil at the same rate as non-magnesian stone, will be

as effective in neutralizing soil acidity, or whether it will exert any deleterious effect on the growth of plants. In experiments conducted by Blair¹ at the New Jersey Experiment Station over a period of 15 years with several kinds of forage crops and vegetables grown on plots limed with non-magnesian limestone in comparison with other crops grown on similar adjacent plots limed with an equal amount of dolomitic limestone, the dolomitic limestone gave as good results on most of the crops as the non-magnesian stone, and in some instances the crop yields on the dolomitic limed plots were greater than those produced on the non-magnesian limed plots. Experiments conducted by Kelly² and other investigators³ are in accord with these findings. The seeds and tissues of plants contain a considerable amount of magnesium. Therefore it is not unreasonable to expect that a soil deficient in calcium might also be deficient in magnesium.

Marl.—Marl is an earthy or clay-like material containing a considerable proportion of calcium carbonate and sometimes magnesium carbonate. The calcium content may vary from 5 to over 95 per cent. Since marl requires no grinding, it is a cheap source of a liming material. However, most marl beds contain too large a proportion of impurities to permit of any but local use. The principal advantage of marl over ground limestone of the same calcium carbonate content is that it occurs naturally in a finely divided state, or it is so soft that it disintegrates when exposed to the weather, and therefore it is only necessary to transport and distribute it on the soil. The particles resulting from the disintegration of marl are usually as small as the smallest particles in ground limestone. It may be more economical to transport a short distance and distribute a low-grade marl than it would be to grind, transport and distribute a high-grade limestone the same or a greater distance. Marls may contain considerable magnesium or be relatively free from it; they may also contain small amounts of phosphorus, potassium and manganese.

Shells.—The shells of mussels, clams and oysters are relatively pure forms of calcium carbonate and yield, upon burning, a high-grade lime; when ground moderately fine they afford an excellent liming material. Small quantities of organic matter, magnesium carbonate and phosphorus are also usually present, and oyster shells may contain traces of fluorine, copper and zinc. Ground shell is prepared in large quantities for use

¹ *J. Am. Soc. Agron.*, **13** (1921).

² *Ibid.*, **9**, 285 (1917).

³ *Rhode Island State College Bull.*, **13** (1918), No. 4, p. 39.

in the poultry industry. The neutralizing value of ground shell is determined by the method described later for limestone. This procedure, however, gives slightly low results unless the organic matter is burned out of the sample before it is treated with acid.

MATERIALS CONTAINING OXIDE AND HYDROXIDE OF CALCIUM

Calcium Oxide, CaO (Lime, Quicklime).—From the standpoint of pure chemistry the term "lime" should apply only to fresh and well-burned calcium oxide. In recent years, however, a tendency to use the term "lime" in its application to agriculture in a loose way has been evident. For example, the phrase "liming the soil" has come to mean the application of either quicklime, slaked lime, limestone, marl, shells or gypsum.

In earlier times, when it became desirable to neutralize acid soils with lime, the freshly burned oxide was usually transported to the field and deposited in small heaps, which were then covered with soil and allowed to remain undisturbed until the slaking process was complete. The slaked heaps were then spread over the soil by means of hand shovels. At the present time air-slaked lime is usually spread on the soil by means of a mechanical spreader. Quicklime becomes hydrated very speedily in the soil, and then changes to carbonate slowly by combining with carbon dioxide.

Calcium oxide or the hydrate is to be preferred to calcium carbonate only when quick action in neutralizing a free acid or aiding in the decomposition of organic matter is the principal object in view, or in localities where a long haul makes the more concentrated form cheaper. In a soil rich in ammonia compounds the finely pulverized limestone is preferable because it avoids the loss of nitrogen. If the final effect desired is only the improvement of the physical properties of the soil and the promotion of nitrification, there is not much difference in the effects produced by calcium oxide and ground limestone.

Hydrated Lime.—When water is added to quicklime it combines to form calcium hydroxide, according to the equation $\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$. If the lime is relatively pure, it will absorb approximately 32.0 per cent of its own weight of water. In recent years mechanical means of hydrating lime have been introduced, whereby it is treated with just enough water to form the hydrate. Lime hydrated by this method is a fine, dry powder, practically all of which will pass a 100-mesh screen. It is packed in paper bags or cloth sacks and will keep indefinitely. This

form of lime is well suited for agricultural purposes and is being used to some extent in regions more or less remote from limestone deposits, because it can be transported in small quantities and it is not subject to the fire hazards of quicklime.

Gas Waste.—Slaked lime is used to absorb hydrogen sulfide, carbon dioxide and other impurities from gas produced by the destructive distillation of coal. The spent product contains the equivalent of about 34 per cent of calcium oxide in the form of calcium carbonate and calcium hydroxide. It also contains much sulfide, sulfite, thiosulfate, thiocyanate and cyanide. Gas lime should be exposed to the air for some time to allow the sulfur compounds to undergo oxidation before it is applied to the soil.

Tannery Waste.—A thick emulsion of hydrated lime is used in the manufacture of leather to remove the hair from hides. The spent material consists of a mixture of calcium carbonate and calcium hydroxide, and it is sometimes used for liming the soil in the vicinity of tanneries.

By-product liming materials should be tested for the presence of substances that might be injurious to the growth of plants. Such substances will include metallic sulfides, sulfurous acid, thiocyanates, cyanides, dicyandiamide and metallic salts. To determine whether any injurious substances are present in liming materials of by-product origin it is best to make a small-scale vegetation test as follows: Mix about 300 grams of medium heavy soil with 2-4 grams of the material; place in small glass vessels of about 10 cm. diameter, moisten, and in each plant about 30 grains of seeds of good viability. As a check, use the same soil alone or mixed with lime known to be non-objectionable. Observe the growth of the plants for about 14 days. Their behavior, according to H. Neubauer,¹ easily discloses the presence of injurious substances.

The degree of purity of caustic liming materials can be judged to some extent by the color of the burned lime. A snow-white appearance indicates a relatively pure product, but a brownish-yellow cast suggests that impurities, including iron, manganese and probably considerable magnesium, may be present.

INDICATIONS THAT A SOIL NEEDS LIMING

A decided acid reaction and failure to grow red clover are good indications that a soil needs liming. Calcium carbonate dissolves in water free from carbon dioxide rather sparingly, about 13 mg. per liter. How-

¹ Methoden zur Bestimmung der Zusammensetzung der Nahrungsmittel der Pflanzen.

ever, when water is saturated with carbon dioxide the solubility of pure calcium carbonate increases thirty-fold, or about 390 mg. per liter. Rain carries the carbon dioxide of the air into the soil, which also contains a considerable amount of this gas, and as the carbonated water percolates soil containing calcium and magnesium carbonates, the soluble bicarbonates of calcium and magnesium are formed. They are removed from the soil in the drainage water. $\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{Ca}(\text{HCO}_3)_2$, $\text{MgCO}_3 + \text{H}_2\text{CO}_3 = \text{Mg}(\text{HCO}_3)_2$.

It is apparent, therefore, that calcium and magnesium carbonates leach from the soil rather rapidly, and it is probably better to make small applications of one to two tons of limestone per acre frequently than to apply larger quantities occasionally. It has been estimated that under ordinary conditions of practical farming the average loss of calcium in the soil may amount to as much as 1,000 pounds of calcium carbonate per acre annually. Leguminous crops remove considerable quantities of calcium from the soil. Red clover and alfalfa remove approximately 100 pounds of calcium carbonate per ton of the dry plant material. In humid regions, therefore, it is necessary to replace calcium in the soil at regular intervals by the addition of some form of the carbonate or oxide.

ANALYSIS OF LIMING MATERIALS

Moisture.—Weigh 0.5 gram of the finely pulverized material into a 15 cc. platinum crucible, heat for 2 hours at 100°C ., cool in a desiccator, and reweigh to determine the percentage of moisture.

Loss on Ignition.—Heat the covered crucible containing the residue from the moisture determination at a moderate red for a few minutes, ignite with a blast burner for 15 minutes, cool in a desiccator, and reweigh to determine the loss on ignition.

Insoluble Material.—Transfer the crucible containing the ignited residue to a 250 cc. porcelain evaporating dish, add hydrochloric acid (1 + 1) until the lime is dissolved, and then add a few cubic centimeters of acid in excess. Rinse the contents of the crucible into the evaporating dish, evaporate to dryness on a hot water bath, and continue to dry on a sand bath until hydrochloric acid is no longer evolved. Cool the dish, add 5 cc. of hydrochloric acid (1 + 1) to the dry residue, and heat for a few minutes on a hot water bath. Then add 25 cc. of hot distilled water and continue the digestion with stirring for about 10 minutes. Filter, and wash the insoluble residue on a quantitative filter, ignite, weigh, and calculate the percentage of insoluble material.

Iron and Aluminum Oxides.—Dilute the filtrate from the insoluble material to about 150 cc., heat to near the boiling point, add a slight excess of ammonia, and continue to heat the beaker for about 5 minutes on the hot water bath. Filter the precipitate and wash thoroughly. Dry, ignite the paper and its contents, and weigh.

This precipitate represents ferric and aluminum oxides and traces of phosphorus. Subtract the weight of the P_2O_5 , as determined by the procedure described below, to obtain the weight of the $Al_2O_3 + Fe_2O_3$. To determine iron, fuse the residue with potassium bisulfate in a platinum crucible. Dissolve the fused mass by heating with 50 cc. of water and 10 cc. of sulfuric acid (1 + 1), reduce the iron with pure zinc, and titrate with 0.1 *N* potassium permanganate. Subtract the weight of Fe_2O_3 from the weight of the $Al_2O_3 + Fe_2O_3$ to obtain the weight of Al_2O_3 .

Calcium.—Evaporate the filtrate from the iron and aluminum precipitate to a volume of about 200 cc., heat to near the boiling point, and while stirring precipitate calcium with the addition of an excess of hot ammonium oxalate. Continue to heat the beaker containing the oxalate precipitate on the water bath for about 1 hour with occasional stirring. Then set the beaker aside and allow it to cool to room temperature. Filter the calcium oxalate and wash. Transfer the precipitate to the same beaker and dissolve it in an excess of hot dilute hydrochloric acid. Dilute to about 150 cc. and add a few drops of ammonium oxalate and ammonia in slight excess, stirring in the meantime. Continue the stirring and heating on the water bath until the calcium oxalate has a granular form and settles quickly after being stirred. Filter the precipitate on a paper or an asbestos pad, in case the precipitate is on paper, thoroughly wash, and strongly ignite to a constant weight in a platinum crucible and calculate the percentage of calcium oxide.

For a volumetric determination of the calcium, filter the oxalate on an asbestos pad, wash pad and precipitate thoroughly with hot water, transfer to a 500 cc. Erlenmeyer flask with about 300 cc. of hot water, and add sufficient sulfuric acid (1 + 1) to dissolve the calcium oxalate. Heat to near the boiling point, titrate with a solution of 0.1 *N* potassium permanganate, 1 cc. of which equals 0.002805 gram of calcium oxide, and calculate the percentage of calcium oxide.

Magnesia.—To the combined washings from the calcium oxalate precipitate, add 10 cc. of concentrated nitric acid and evaporate to dryness. Take up the residue in a few cubic centimeters of hydrochloric acid and water, transfer to a 100 cc. beaker, make alkaline with ammonia, cool, and precipitate magnesium with a slight excess of sodium phosphate solution and with vigorous stirring. Make the solution strongly ammoniacal and allow to stand for about 6 hours under a bell jar, then filter the precipitate on a quantitative filter paper, wash with a dilute solution of ammonia, ignite strongly in a porcelain crucible, weigh as magnesium pyrophosphate, and calculate the percentage of magnesium oxide. Dissolve the magnesium pyrophosphate precipitate in nitric acid and test for manganese with periodate; if present, determine by the periodate method as described below and make correction.

Manganese.—Limestones contain an appreciable amount of manganese, which is determined as follows:

Weigh 5 grams of the finely powdered limestone into a platinum or porcelain crucible and ignite to destroy organic matter; cool, dissolve by the addition of an excess of nitric acid (1 + 1) and a few cubic centimeters of hydrogen peroxide, transfer to a 150 cc. beaker, and boil. Filter out and wash the insoluble residue. Transfer the filtrate to a 150 cc. Erlenmeyer flask, add 5 cc. of concentrated nitric acid and about 0.01 gram of potassium periodate, and boil until the permanganic acid color develops; continue to heat on the water bath for 1 hour, cool, make to a

definite volume, remove an aliquot and compare with a manganese standard in Nessler tubes or a colorimeter.

Prepare the standard permanganate solution as follows: Dissolve 0.2877 gram of pure potassium permanganate in a small quantity of water, add an excess of sulfuric acid, reduce carefully with hydrogen peroxide, and make up to 1 liter. One cubic centimeter of this solution is equivalent to 0.1 mg. of manganese. To develop the permanganate color add, in a measured portion of the standard, a small quantity of potassium periodate and boil as with the sample.

Copper.—The small quantities of copper and zinc that occur in limestones can be determined as follows:

Dissolve 1000 grams of freshly broken stone in pure hydrochloric acid, dilute to a volume of about 6 liters, heat to near the boiling point, make the solution distinctly alkaline with ammonia, and saturate it with hydrogen sulfide. After allowing the combined sulfides of iron, copper and zinc and the aluminum hydroxide to settle, syphon off the clear supernatant solution, filter, and wash the black precipitate with dilute ammonium sulfide to free it from calcium chloride. Then transfer the filter containing the precipitate to a porcelain dish and dissolve the iron and zinc sulfides and aluminum hydroxide by the addition of 0.25 *M* hydrochloric acid, stirring and macerating the filter until only a small black precipitate of copper sulfide, adsorbed for the most part on the filter paper, remains. Filter the paper pulp out, wash, dry and ash; dissolve the ash in hydrochloric acid, precipitate iron and aluminum with the addition of ammonia, filter, and wash. Evaporate the filtrate to dryness, and take up in a few drops of hydrochloric acid. Make the solution to about 50 cc., precipitate the copper with hydrogen sulfide, filter, wash, and ignite. Dissolve the copper oxide in a few drops of nitric acid, filter, wash, and evaporate the filtrate to dryness in a small porcelain dish. Dissolve the residue in a small drop of dilute nitric acid, make to a volume of 50 cc., and mix. Transfer to a Nessler jar 10 cc. of the copper solution and 10 cc. of a fresh 0.1 per cent water solution of potassium ethyl xanthate, dilute to 25 cc. with water, and mix. Then transfer to a second Nessler jar 10 cc. of the xanthate solution and dilute to a volume of about 15 cc.; add a solution of copper nitrate containing 0.0001 gram of copper per cubic centimeter dropwise, mixing with a glass stirring rod until the color in the standard tube matches the color in the tube containing the sample. Dilute the volume with water to 25 cc. and make the final adjustment of the color by the addition of a few drops of the standard copper solution, noting the quantity of the copper solution required to match the sample, and calculate the percentage of copper.

Zinc.—Boil the solution containing the principal part of the iron, aluminum and zinc with 10 cc. of strong nitric acid to oxidize ferrous compounds. Precipitate the iron and aluminum by the addition of ammonia, filter, and wash. Discard the precipitate. Evaporate the filtrate to a small volume, acidify with acetic acid, and precipitate the zinc with hydrogen sulfide. Filter the precipitate, and absorb on a pad of paper pulp; then wash with a dilute solution of ammonium acetate saturated with hydrogen sulfide, and burn. Dissolve the zinc oxide in a drop or two of dilute

hydrochloric acid, transfer to a 50 cc. volumetric flask, dilute to the mark, mix, and determine zinc by the turbidity ferrocyanide method, as follows:

Transfer a 5 cc. aliquot of the zinc solution to a Nessler jar containing 5 cc. of a freshly prepared 0.2 per cent solution of potassium ferrocyanide. Dilute with water to 50 cc. and mix. Dilute 5 cc. of the 0.2 per cent solution of ferrocyanide, which has been placed in another Nessler jar, to about 40 cc., and add dropwise and with stirring a standard zinc solution, 1 cc. of which contains 0.001 gram of zinc, until the turbidity in the jar containing the standard matches the turbidity in the jar containing the sample. From the amount of the zinc standard required calculate the percentage of zinc.

Phosphorus.—Most limestones contain an appreciable amount of phosphorus. It may be determined as follows:

Dissolve 1–5 grams of the pulverized material in hydrochloric acid (1 + 1) and about 1 cc. of nitric acid. After effervescence has ceased, boil the solution for about 3 minutes. Filter out the insoluble residue and wash. Make the filtrate alkaline with a slight excess of ammonia and redissolve the precipitate by the addition of nitric acid drop by drop. Place the flask in a bath held at 60° C. and precipitate and determine phosphorus according to the volumetric method described under fertilizers in *Methods of Analysis, A. O. A. C.*

Carbon Dioxide, CO₂.—Many forms of apparatus have been devised for the determination of carbon dioxide in limestones or other calcareous materials. They may be divided into three groups according as the carbon dioxide is determined by (1) absorbing the evolved gas in an alkaline reagent and determining its increase in weight, (2) measuring the volume of the gas, and (3) noting the loss in weight of the sample when treated with a known weight of acid.

For the accurate determination of carbon dioxide the Knorr apparatus, as illustrated in *Methods of Analysis, A.O.A.C.*, and in Fig. 78, Vol. I, is considered to be the most satisfactory. The carbon dioxide is set free in this apparatus by digestion with hydrochloric acid and determined gravimetrically by absorption in soda lime or potassium hydroxide solution. The directions given in *Methods of Analysis* on the use of this apparatus for the determination of carbon dioxide in baking powders are applicable to the same determination in liming materials. Many types of absorption bulbs, as illustrated in the catalogues of various chemical supply houses, are now in use but the Geissler absorption bulb shown in connection with the Knorr apparatus in the figures referred to is still popular among many analysts. The Bowen bulb and the Schmitz drying tube may also be conveniently used as containers for the concentrated sulfuric acid used in drying the gas.

The volumetric method of determining carbon dioxide by measuring the volume of the evolved gas is more rapid than the Knorr gravimetric method and gives fairly accurate results. The improved Parr apparatus,

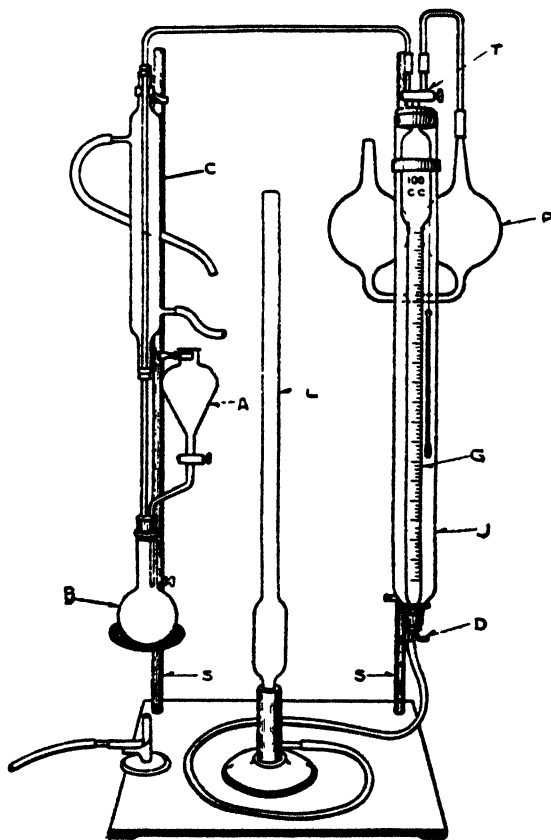


FIG. 1 --Parr Apparatus

Fig. 1, is particularly well adapted for use in this determination. The procedure is as follows:

Fill the jacket tube *J* with water slightly acidulated to keep it clear and the leveling tube *L* with water containing 2 or 3 cc. of sulfuric acid and a few drops of methyl orange, the latter being added to impart color and facilitate readings. Connect the inlet *D* with air pressure and adjust so that 2 or 3 bubbles of air per minute pass through the water in *J*, thus keeping its temperature equalized. Fill the large double pipet *P* half full with 40 per cent potassium hydroxide. Connect *P*

with the buret *G* through the three-way cock *T* and lower the leveling tube *L* until the liquid in *P* rises in the capillary tube to the mark on the right limb. Now close cock *T* to *P*, open it to the tube running to the flask *B* and raise the leveling tube *L* until the liquid in *G* rises to the cock, completely filling the buret. Close cock *T* to keep the liquid in *G* at the zero point. Place 1-5 grams of the sample, according to its richness in carbonates, in the flask *B* and add about 50 cc. of water. Connect the flask with funnel *A* and bring the ring support with wire gauze in place under the flask. Open the cock at the lower end of the funnel and boil the contents of the flask 3 or 4 minutes to drive out the air. Remove the flame and at once close the funnel cock, forming a partial vacuum in the flask, since cock *T* is also closed. Add from *A* concentrated hydrochloric acid drop by drop to *B* by lowering the leveling tube *L* and opening the cock *T* to the tube connecting with *B*, taking care not to admit any air through the opened cock of *A*. When the evolved gas nearly fills the graduated buret *G*, shut off the flow of acid from *A*, close the cock *T* and read the volume of the gas after bringing the surfaces of the liquid in *L* and *G* exactly on a level. Also note the temperature of the jacket water and the barometric pressure. Now open *T* to the capillary and force the gas in *G* completely into *P* where it is held by closing *T* again and left for complete absorption of the carbon dioxide. Adjust the liquid in *G* to the zero point again and continue the evolution of gas, repeating the measurements and expulsions of the gas in *P* until no more carbon dioxide is evolved. Finally boil the liquid in *B* a few minutes and, after removing the flame, add hot water through *A* until the solution nearly reaches the stopper and no water remains in *A*. Lower the leveling tube *L*, drawing air through *A* into *B* and sweeping out the residual gas in the connecting tubes until the volume of air drawn into *G* is slightly more than 100 cc. Transfer this air to the bulb *P* for final absorption of the remaining carbon dioxide. Return all the unabsorbed gas (air) from *P* to *G* and read its volume. Take the difference between this volume and the total of the several volumes (all corrected for water vapor and brought to standard conditions of temperature and pressure) as the volume of the carbon dioxide contained in the sample.

The Schroedter apparatus shown in Fig. 2 is one of several forms that are in use for determining carbon dioxide in a material by the decrease in weight that follows treatment with an acid. The method of using the apparatus is as follows:

Place 0.5-1.0 gram of the sample in the bottom of the flask and fill the bulbs as indicated in the figure about two-thirds full with dilute hydrochloric and strong sulfuric acids. Weigh the apparatus as thus charged and then allow the hydrochloric acid to flow down slowly into the sample without removing the stopper from the hydrochloric acid bulb. The evolved gas escapes through the strong sulfuric acid, but loss of water vapor is prevented by absorption in the acid. When effervescence has ceased, heat the solution to boiling and boil very gently for about 3 minutes. Connect a soda lime tube to the hydrochloric acid bulb and by applying gentle suction at *A* aspirate a slow current of air through the soda lime tube and the apparatus until it is cold in order to expel all carbon dioxide. Again stopper and weigh, the loss in weight being taken as the CO_2 in the sample.

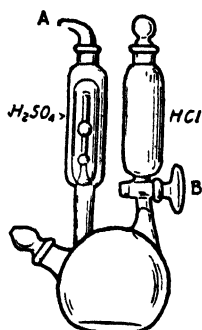


FIG. 2.—Schroedter Apparatus.

This method is a convenient one for use in the approximate valuation of materials containing carbonates, but it is not adapted to the determination of small quantities of carbon dioxide.

Caustic Value of Quick and Hydrated Lime.—Shaw, MacIntire and Underwood¹ have recently published a method for determining the caustic value of calcium oxide and hydrated lime. The method is somewhat complicated and requires a drawing for the set-up of the apparatus. (See Fig. 3). The following is a brief outline of the method:

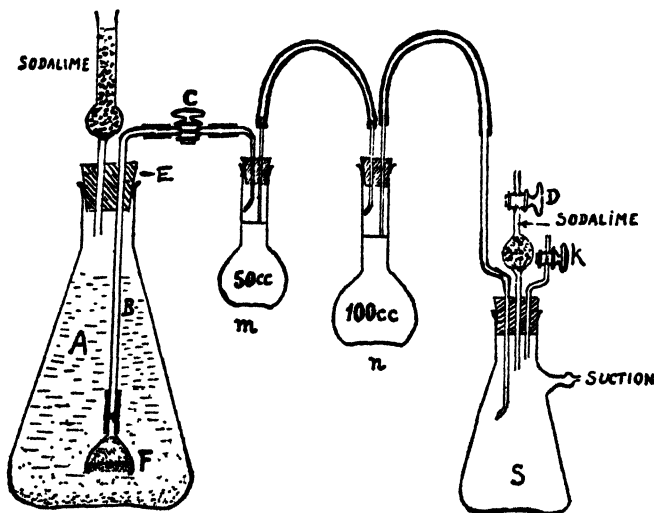


FIG. 3.—Shaw-MacIntire-Underwood Device.

¹ *Ind. Eng. Chem.*, **20**, 212 (1928), which see for detailed description of method and apparatus.

Grind the sample to pass a 100-mesh sieve, avoiding undue exposure to moist air. Weigh accurately about 1.5 grams (preferably from a weighing tube by difference) into a 500 cc. Erlenmeyer flask fitted with a tight rubber stopper. Dissolve 25 grams of granulated sugar in cold CO₂-free water in a flask graduated to deliver 500 cc., make to volume, and pour this solution upon the lime portion slowly, shaking to keep the lime from forming lumps. Stopper the Erlenmeyer flask securely and shake well. (Clean dry glass beads may be added to aid in disintegrating the lumps.) Shake 6 times for 1 minute, 2 or 3 minutes apart; allow to stand 15 minutes longer and filter quickly with as little exposure to air as possible. Titrate 50 cc. of the clear solution with 0.5 *N* hydrochloric acid and phenolphthalein. Measure twice the number of cubic centimeters of 0.5 *N* hydrochloric acid required into a 250 cc. Erlenmeyer flask, run into it 100 cc. of the clear solution, and finish the titration. The number of cubic centimeters required by the 100 cc. aliquot, multiplied by 7 and divided by the weight of sample taken, gives the percentage of calcium oxide in the sample uncombined or as hydroxide. The presence of magnesia does not vitiate the result. For a filtering apparatus which avoids contact with air, and more details of the procedure, see the article cited.

NEUTRALIZING VALUE OF LIMING MATERIALS

The calcium and magnesium content of limestones and marls varies widely, and therefore a method for the approximate determination of their neutralizing value for agricultural use is desirable. The following method is used at the Kentucky Agricultural Experiment Station for the determination of the neutralizing value of liming materials.

Weigh 0.5 gram of the finely pulverized material and transfer into a 150 cc. Erlenmeyer flask; add 25 cc. of 0.5 *N* hydrochloric acid to the flask by means of a pipet and heat the flask gently until effervescence has ceased (about 3 minutes). Cool the flask, rinse down the sides with distilled water, add a few drops of methyl orange indicator, and then add standard sodium hydroxide from a buret until the end point is reached. From the quantity of sodium hydroxide required compute the number of cubic centimeters of 0.5 *N* acid consumed in decomposing the limestone. This figure multiplied by 5 (that is, 200×0.025) gives the neutralizing value estimated as percentage of CaCO₃.

The relative neutralizing values of pure liming materials, as calculated from their formulas and on the basis that pure calcium carbonate has a neutralizing value of 100, are given in Table I.

TABLE I.—RELATIVE NEUTRALIZING VALUE OF LIMING MATERIALS CALCULATED ON THE BASIS OF A VALUE OF 100 FOR PURE CALCIUM CARBONATE.

Pure liming materials	Relative value
Calcium carbonate	100
Calcium oxide, quicklime	179
Calcium hydroxide, hydrated lime	135
Dolomitic limestone	108
Dolomitic quicklime	207
Dolomitic hydrated lime	151

Fineness of Ground Limestone.—The rapidity with which the acidity in a soil is neutralized by an application of ground limestone depends upon its degree of fineness and the thoroughness with which it is mixed in the soil.

A good grinding of limestone for agricultural use is approximately as follows:

	Per cent
Held on the 10-mesh sieve	10
Held on the 40-mesh sieve	35
Held on the 80-mesh sieve	15
Passed the 80-mesh sieve	40
Total	100

TABLE II.—PARTIAL ANALYSIS OF MATERIALS CONTAINING CALCIUM.
(Results expressed in percentage)

	SiO ₂ sand, etc.	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	CaF
Limestone	0.74	0.11	0.04	54.96	0.54	0.03	0.02	—
Limestone argillaceous	21.28	2.79	4.11	37.24	1.51	.55	—	—
Dolomite	7.50	1.44	3.26	28.60	16.65	—	—	—
Marl	19.90	—	—	80.1 *	—	—	—	—
Gypsum	—	—	—	32.56	—	—	46.51	—
Superphosphate	—	—	—	30.73	—	—	29.14	—
Rock phosphate	4.50	3.12	.70	41.44	—	35.00	—	6.42
Basic slag	7.84	19.06	—	49.84	4.66	15.87	—	—
Caustic lime, CaO	—	—	—	90-98	—	—	—	—
Magnesium lime	—	—	—	55-85	10-40	—	—	—
Oystershell lime	—	—	—	85-95†	—	—	—	—
Slaked lime	—	—	—	75.7 ‡	—	—	—	—
Bone meal	—	—	—	37.2	—	31.0	—	—
Nitrolime	—	—	—	64.79	—	—	—	—
Gas lime	—	—	—	34.08	—	—	—	—

* Neutralizing value expressed as CaCO₃.

† Neutralizing value of raw shells 90 95 per cent, expressed as CaCO₃.

‡ 24.3 per cent H₂O.

II.—MATERIALS CONTAINING SULFATE

Gypsum, superphosphate, ammonium sulfate, potassium sulfate and manganese sulfate are sources of sulfur for soils, although the addition of sulfur is not the primary purpose for which these materials are added to the soil.

Gypsum (Land Plaster), CaSO₄·2H₂O, is a common mineral. It is found in extensive beds in limestone regions and in clay deposits. In the early days of agriculture in this country, land plaster was used extensively as a fertilizer; the results were good especially when it was applied to

clover and used in connection with manure. Applications not exceeding 200 pounds to the acre were effective. The beneficial effect of gypsum upon the root nodules and the free nitrogen fixing bacteria in the soil, or the addition of a needed sulfur compound, may have been the cause of the increased yields. The general use of superphosphate at the present time, however, probably has rendered the use of gypsum for this purpose unnecessary, because more than half of the weight of the ordinary superphosphate is gypsum. The old explanation that the application of gypsum benefitted a crop by liberating potash in the soil seems not to have been borne out by experimental evidence. In arid regions gypsum is used to correct "black alkali," which is caused by sodium carbonate in the soil. Gypsum reacts with sodium carbonate to produce sodium sulfate and calcium carbonate, substances not so inimical to plant growth as sodium carbonate.

Superphosphate.—In 100 pounds of completed superphosphate there are approximately 58 pounds of hydrated calcium sulfate and 42 pounds of soluble calcium phosphate. Owing to the presence of calcium carbonate and calcium fluoride in the raw rock phosphate, a larger quantity of calcium sulfate may often be found. Superphosphate may therefore be considered as a source of gypsum. The proportion of gypsum in superphosphate may be determined approximately from the total sulfate sulfur content as in gypsum, and by calculating the equivalent weight of hydrated calcium sulfate.

Ammonium Sulfate, $(\text{NH}_4)_2\text{SO}_4$, when pure, contains 21.2 per cent of nitrogen and 24.26 per cent of sulfur. The commercial product used in fertilizers usually contains slightly lower quantities of nitrogen than the pure compound. Ammonium sulfate is a by-product resulting from the manufacture of coke and illuminating gas. The nitrogen content of coal varies considerably and the quantity of ammonium sulfate recovered ranges from 8 to 25 pounds per ton of coal.

Ammonium sulfate may contain small amounts of impurities such as sand, salt, moisture and tarry matter, which impart a brown color and a characteristic odor to the salt but do not affect its value as a fertilizer. Some samples may exhibit a bluish tint, which is due to traces of ferric ferrocyanide (Prussian blue).

Ammonium sulfate that has been obtained from gas liquors may contain small quantities of thiocyanates and also, rarely, cyanides. These

compounds are to be considered plant poisons.¹ The presence of thiocyanates can be detected by the characteristic red color produced in an alcoholic extract of the salt by the addition of a few drops of a dilute solution of ferric chloride.

To detect cyanides add an excess of potassium hydroxide to a concentrated solution of the ammonium sulfate, then add a few drops of ferric and ferrous salts and boil. The formation of Berlin blue upon the addition of hydrochloric acid indicates cyanides. Sodium sulfate, sodium chloride and gypsum have been found as adulterants in ammonium sulfate. Two very simple tests can be made to detect impurities in ammonium sulfate: (1) Any insoluble residue that remains when a portion of the salt is stirred in water is an impurity; (2) any non-volatile substance that remains when the salt is heated to redness is also an impurity. If the proportion of insoluble or non-volatile matter appears unduly large such a sample should be regarded with suspicion and a determination of ammonia should be made.

When ammonium sulfate is applied to the soil the ammonia is oxidized to nitric acid, which leaves sulfuric acid to combine with any basic material present. If the soil contains calcium and magnesium carbonates, the sulfuric and nitric acids combine with them, forming the sulfates and nitrates of these elements. The continued application of ammonium sulfate to the soil without the use of a corresponding amount of basic material will result ultimately in the production of acid conditions in the soil $[(\text{NH}_4)_2\text{SO}_4 + 4\text{O}_2 = \text{H}_2\text{SO}_4 + 2\text{HNO}_3 + 2\text{H}_2\text{O}]$.

Potassium Sulfate, K_2SO_4 , is known commercially as sulfate of potash. When pure it contains 44.8 per cent of potassium and 18.4 per cent of sulfur. The commercial product usually contains small quantities of sulfates of calcium, magnesium, and sodium.

Manganese Sulfate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.—In recent years it has been shown by McHargue that manganese is an essential element for the normal growth of plants and has an important function in the synthesis of chlorophyll.² It has also been shown by Schreiner and Dawson³ that a few large areas of soil in this country, deficient in available manganese, show a response in the growth of crops when an adequate quantity of an available manganese compound is added to the soil. Manganese sulfate applied at the

¹ Feilitzen, *Fühling's Landw. Zts.*, **61**, 285 (1912); Hoselhoff, *Zentr. Agr. Chem.*, **33**, 24 (1905).

² *Ind. Eng. Chem.*, **18**, 172 (1926). For the early work of Bertrand and other investigators upon Mn, Zn, B, Ni, Co, I, and other minor mineral constituents, see bibliographic references on these elements.

³ *Ibid.*, **19**, 400 (1927).

rate of about 50 pounds per acre is the compound most commonly used. Experiments at the Kentucky Agricultural Experiment Station show that plants can also utilize manganese carbonate and dioxide as sources of manganese in sand cultures.

Ferrous Sulfate (Copperas) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.—The addition to the soil of a small quantity of ferrous sulfate as a stimulant for the growth of plants was formerly recommended, the idea being that a readily available form of iron was needed, but it is now generally assumed that soils well supplied with organic matter have the necessary amount of iron to provide for the normal growth of plants. However, with the development of chlorosis in certain important plants, including pineapples, sugar cane and fruit trees, reports are on record where a normal green color and normal growth have been restored by spraying the chlorotic plants with a dilute solution of ferrous sulfate. Since it has been demonstrated that manganese functions in the synthesis of chlorophyll and since iron compounds are usually contaminated with manganese, it is quite probable that manganese, as well as iron, is a factor in restoring normal green color and growth to chlorotic plants.

A solution of ferrous sulfate in water has been used effectively to kill certain weeds, such as wild mustard in growing grain or grass. A solution just strong enough to kill the broad-leaf weeds may be sprayed on without serious injury to the grasses. Two pounds to the gallon is the strength recommended.¹

ANALYSIS OF MATERIALS CONTAINING SULFATE

Total Sulfate Sulfur.—Weigh 1 gram of the finely ground material containing sulfates and transfer to a 250 cc. beaker. Add about 200 cc. of hot distilled water and 20 cc. of hydrochloric acid (1 + 1); place the beaker on the hot water bath and stir occasionally until practically all the material is dissolved. (It may require an hour or more to bring gypsum into solution. If the insoluble material is small, light in weight and flocculent, it is not gypsum. However, if a light-gray residue that settles quickly remains in the center of the beaker when the solution is stirred in one direction for a few seconds and there is no grit or sand detected with the stirring rod, it is an indication of undissolved gypsum, which may be brought into solution by further digestion and stirring.) Filter the insoluble residue and wash. Cool the filtrate, transfer to a 100 cc. volumetric flask, make to the mark, and mix. Take an aliquot of 10 cc., heat to near the boiling point, and precipitate sulfates with an excess of barium chloride. Cool, filter the precipitate of barium sulfate, wash, ignite, weigh, and calculate the percentage of the original compound.

¹ New York Agr. Expt. Sta. Bull., 466, p. 53.

Free Acid in Ammonium Sulfate.—Weigh 1 gram of the salt into a beaker, dissolve in water, and titrate the free acid with standard alkali, using methyl orange as an indicator. Calculate the percentage of sulfuric acid.

Thiocyanates in Ammonium Sulfate.—Dissolve 5 grams in water, boil, add a little sodium bisulfite, and titrate with a copper sulfate solution containing 6.24 grams of cupric sulfate per liter, until one drop colors potassium ferrocyanide paper brown (touch drop method). One cubic centimeter of cupric sulfate solution corresponds to 0.00145 gram of thiocyanate ion, or 0.00190 gram of ammonium thiocyanate.

Manganese in Manganese Sulfate.—Weigh 1 gram of manganese sulfate, dissolve in water, dilute to 100 cc., mix, and transfer an aliquot of 10 cc. to a beaker. Add 5 cc. of dilute sulfuric acid (1 + 1) and 0.01 gram of potassium periodate and boil until the purple color of permanganic acid develops. Determine manganese according to the directions given for the determination of manganese in liming materials.

Ferrous Iron in Ferrous Sulfate.—Dissolve 1 gram of the salt in dilute sulfuric acid (1 + 1), dilute to 100 cc., mix, titrate a 10 cc. aliquot of the solution with 0.1 N permanganate solution, and calculate the result for iron to ferrous sulfate.

III.—MISCELLANEOUS CONSTITUENTS OF POTASSIC FERTILIZERS

Agricultural crops show considerable variation in the amount of potassium they remove from the soil. Tobacco, sugar beets, sugar cane and most of the legumes remove relatively large quantities, and any deficiency of available potassium in the soil may seriously affect the yield of these crops. However, a natural deficiency of potassium in the soil is of comparatively rare occurrence in this country, and under ordinary conditions of farming a large proportion of the potassium taken from the soil in the crops is returned in manures.

The principal sources of the potash salts used for fertilizer purposes are the natural salt deposits of Germany and France. The potash occurs in these deposits in the form of definite minerals, of which the most important are carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sylvinite ($x\text{KCl} \cdot y\text{NaCl}$), glaserite ($x\text{K}_2\text{SO}_4 \cdot y\text{Na}_2\text{SO}_4$), and kainite ($\text{MgSO}_4 \cdot \text{KCl}_3 \cdot \text{H}_2\text{O}$). These occur in association with many other salts such as halite (NaCl), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), glauberite ($\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$) and boracite ($2\text{Mg}_3\text{B}_5\text{O}_{15} \cdot \text{MgCl}_2$).

An annual production of about 90,000 tons of potassium chloride is now being obtained from the brine of Searles Lake, Calif. Smaller quantities have been, or are being produced from other sources in this country, such as alunite, wood ashes and kelp, or as a by-product in the cement, blast furnace, industrial alcohol and tobacco industries.

Potassium Salts.—Detailed information on the occurrence and composition of commercial potash salts are given in the chapter on Potash Fertilizers. Other elements than the potassium contained in potash salts may at times merit serious consideration. Thus severe injury to crops has resulted from the application of fertilizers in which potash salts containing boron formed an ingredient. It is also recognized that the presence of chlorine in fertilizers used on tobacco has a deleterious effect upon the burning quality of the tobacco.

Tobacco Trash, Stems and Stalks.—The waste materials resulting from the harvesting and manufacture of tobacco contain considerable quantities of the important fertilizer constituents, nitrogen, potassium, calcium and phosphorus, which should be conserved and utilized for agricultural purposes. The percentages are subject to wide variation, as shown in the following table.

	N	P ₂ O ₅	K ₂ O	CaO
Tobacco leaves	4.14	0.77	4.45	4.00
Tobacco stems	2.50	1.00	6.00	—
Tobacco stalks	3.50	0.79	4.40	2.00

Kelp.—That certain species of seaweed have value for fertilizer purposes has long been known. They have been used for such purposes in European countries and along the New England and the Pacific coasts in the United States. It is stated that the giant kelps of the Pacific coast are essentially different from the Atlantic kelps in that the potassium content is higher and the iodine content lower. The dried kelps from the Pacific coast may contain 30 per cent or more of potassium chloride. Notwithstanding the well-known fact that kelp contains a relatively large quantity of potassium and other important fertilizer constituents, including calcium, magnesium, manganese, copper, iodine and zinc, thus far it has not been utilized on a large scale for the manufacture of fertilizers. This fact indicates that the cost of harvesting and preparing the material for the market is probably too great for a profit.

Wood Ashes.—The only kind of ashes used for fertilizer purposes are those derived from the burning of hard woods. The quantity of potassium salts obtained from this source, however, constitutes a very small part of the total amount used in agriculture and other industries. The fertilizer constituents in wood ashes, calcium, magnesium, phosphorus and manganese may be of enough importance to warrant quantitative determinations.

The constituents of wood ashes may be determined according to the directions given in *Methods of Analysis, A.O.A.C.*, for the analysis of plant ashes.

DETERMINATION OF MISCELLANEOUS CONSTITUENTS OF POTASSIUM SALTS

Sodium.—Boil 25 grams of the potassium salt with 100 cc. of water, filter, wash the residue with hot water, and bring the filtrate and washings to 500 cc. Acidify 200 cc. of the filtrate with hydrochloric acid, boil, and completely remove the sulfuric acid by precipitation as barium sulfate in a 500 cc. flask without using an excess of barium chloride. Bring to volume, mix, settle, and evaporate 50 cc. of the solution to dryness to remove hydrochloric acid. Add oxalic acid, ignite to decompose the magnesium chloride, moisten the residue with a little ammonium carbonate to convert any lime to calcium carbonate, extract the residue with water to obtain the alkali chlorides, evaporate to dryness, drive off the ammonium salts by gentle ignition and weigh. Determine the potassium and subtract the weight of the potassium chloride from the weight of the alkali chlorides to obtain the sodium chloride. Calculate to sodium.

Calcium.¹—Dissolve 10 grams of the salt in water in a 500 cc. flask, add twice normal carbonate-free sodium hydroxide at ordinary temperature to precipitate the magnesium, fill to the mark, shake, filter, and precipitate the calcium in 250 cc. of the filtrate with ammonium oxalate. Proceed as described in the analysis of liming materials.

Magnesium.²—Boil 10 grams of the salt not less than 1 hour with about 350 cc. of water in a 500 cc. flask. Cool, and add 60 cc. of twice normal sodium hydroxide and, in case of a high calcium content, 20 cc. of a neutral solution of potassium oxalate (1 + 10). Fill to the mark, shake, let stand 15 minutes, while the flask remains closed, and filter. Titrate 50 cc. of the filtrate with 0.1 *N* hydrochloric or sulfuric acid. Subtract the number of cubic centimeters of acid required from 120 and calculate the difference to percentage of magnesium in 1 gram of salt.

Sulfates.³—Dissolve 5 or 10 grams of the salt in water, filter, boil, add barium chloride dropwise, and proceed as directed under total sulfate sulfur, p. 449.

Chlorine.—Titrate a neutral solution of the salt with 0.1 *N* silver nitrate, using potassium chromate (1 + 10) or neutral sodium arsenate⁴ as indicator, as directed in the chapter on Waters, Brine and Salt, *Methods of Analysis, A. O. A. C.*

Boron.—Proceed as directed in the chapter on Fertilizers, *Methods of Analysis, A. O. A. C.*

¹ Tietjens, *Laboratoriumsbuch für die Kaliindustrie*, p. 26.

² Precht, *Z. anal. Chem.*, **18**, 438 (1879).

³ Ruppin, *Chem.-Ztg.*, **33**, 17, 398 (1909).

⁴ Lunge, *Z. angew. Chem.*, **10**, 549 (1896).

IV.—MISCELLANEOUS CONSTITUENTS OF PHOSPHATIC FERTILIZERS

Rock Phosphate.—A good grade of rock phosphate contains the equivalent of about 40 per cent of calcium oxide (CaO), which makes it an indirect source of calcium in a soil deficient in this element. Rock phosphate may contain varying amounts of calcium carbonate and fluoride in addition to the calcium in combination with phosphorus.

Bones.—Fresh bones contain about 65 per cent of tricalcium phosphate and 35 per cent of organic matter in the form of fat and gelatin. To remove the fat and gelatin, raw bones are steamed in tanks under a pressure of about 40 pounds. The fat and gelatin are removed for further treatment, and the bones are dried and ground to produce "steamed bone meal." This material is added to the soil as a source of phosphorus and, like rock phosphate and superphosphate, it contains calcium equivalent to about 37.0 per cent of calcium oxide (CaO).

Basic Slag.—A good grade of basic slag contains the equivalent of about 50 per cent of calcium oxide; it also contains some free caustic lime, considerable calcium silicate, and a small quantity of calcium carbonate, all of which have the property of neutralizing acidity in soils. The superior beneficial effect of basic slag on the soil, as compared with superphosphate, has long been recognized in agricultural practice. When applied in liberal amounts to heavy clay soils, basic slag produces physical changes which render the soil loose, similar to the effects produced with lime and limestone. The basic slag manufactured in the Birmingham district contains about 3.0 per cent of manganese, which may be a contributing factor in the fertility of soils deficient in manganese. The Birmingham district is the only source of basic slag in this country at the present time.

Superphosphate.—This material is made by treating rock phosphate or bone meal with sulfuric acid. The resulting product contains approximately 60 per cent of calcium sulfate and 40 per cent of soluble calcium phosphate and is therefore an indirect source of calcium and sulfur for soils.

DETERMINATION OF MISCELLANEOUS CONSTITUENTS OF PHOSPHATIC MATERIALS

ROCK PHOSPHATE

Moisture.—The sample should be ground fine enough to pass a 100-mesh sieve.

Weigh 2 grams in a tared platinum crucible, place in an air bath at 105° C. and heat for 3 hours. Place the lid on the crucible, cool in a desiccator, and weigh. The loss in weight is moisture.

Organic Matter.—Determine the organic matter according to Wyatt,¹ as follows:

Transfer the portion used in the moisture determination to a platinum crucible, gradually heat to full redness in a Bunsen flame, and then ignite over the blast-lamp. Repeat this operation with alternate weighings until a constant weight is obtained. The loss (after deducting the percentage of carbon dioxide and moisture as found in other portions) may be taken as organic matter.

This method is adequate for all practical purposes, but when minerals containing fluorine are strongly ignited, a part of the fluorine is expelled; hence, if more accurate determinations are required, the loss of fluorine must be taken into account. It has been proved that a pure calcium fluoride undergoes progressive decomposition at a bright red heat with formation of lime.

Calcium.—Weigh 10 grams of the finely powdered sample into a beaker, add 10 cc. of hydrochloric acid (1 + 1) and 5 cc. of nitric acid (1 + 1); cover with a watch-glass; and digest on a hot water bath, with occasional stirring, for about 30 minutes. Filter out the insoluble residue, wash thoroughly with hot distilled water, dry, ignite, weigh, and calculate the percentage of insoluble matter. Transfer the filtrate to a 200 cc. volumetric flask, cool, make to the mark, and mix. Transfer an aliquot of 5 cc., equivalent to 0.25 gram, to a 250 cc. Erlenmeyer flask; dilute to about 100 cc. with cold distilled water; and add a few drops of alizarine sulfonate indicator and then ammonia drop by drop with shaking until the solution is slightly alkaline, as shown by a change in the indicator from orange to pink. Add 10 cc. of 0.5 N hydrochloric acid, and then 10 cc. of a 2.5 per cent solution of oxalic acid. Further dilute the solution to about 200 cc. with hot water and heat to the boiling point. Add an excess of a saturated solution of ammonium oxalate drop by drop, while rotating the flask over a heated wire gauze, until all the calcium has been precipitated and has assumed a granular form. Set the solution aside to cool at room temperature, add 8 cc. of a 20 per cent solution of sodium acetate, agitate the solution, and allow to stand for about 2 hours. Filter the calcium oxalate on an asbestos pad and wash thoroughly with cold distilled water. Transfer the calcium oxalate and the asbestos pad to a 250 cc. Erlenmeyer flask, add 10 cc. of dilute sulfuric acid (1 + 1), heat to near the boiling point, and titrate with 0.1 N potassium permanganate (1 cc. = 0.002805 gram of CaO). Calculate the percentage of calcium oxide.

Calcium (Gladding Method).²—Boil 5 grams of the finely ground rock phosphate for 30 minutes in 50 cc. hydrochloric acid (1 + 1), filter into a 250 cc. volumetric flask, and add 10 cc. of hydrogen peroxide solution; boil for a few minutes

¹ *Phosphates of America*, 4th ed., 145 (1892).

² *J. Ind. Eng. Chem.*, 1, 249 (1909).

to oxidize any ferrous iron and expel oxygen, cool, fill to the mark, and mix. Transfer 25 cc. ($\frac{1}{2}$ gram) to a 250 cc. Erlenmeyer flask; dilute to 100 cc., heat to boiling, and add ammonia to a slight alkalinity, then hydrochloric acid (1 + 1) drop by drop from a pipet until the ammonia precipitate just redissolves, then a hot saturated solution of ammonium oxalate from a pipet until all the calcium is precipitated and about 10 cc. in excess; cool, filter off the calcium oxalate on an asbestos pad held in a Caldwell crucible, wash with hot water until free of chlorides, transfer the precipitate and the asbestos pad into the Erlenmeyer flask in which it was precipitated, add 10 cc. of sulfuric acid (1 + 1), heat to nearly boiling, titrate with 0.1 *N* potassium permanganate (1 cc. = 0.002005 gram of Ca), and calculate the percentage of calcium.

Iron and Aluminum.—Transfer the filtrate from the calcium oxalate to a 500 cc. Kjeldahl flask, add 5 cc. of concentrated sulfuric acid, and evaporate to white fumes by boiling to destroy the excess of oxalic acid. Cool slightly, add 50 cc. of water and 10 cc. of hydrochloric acid (1 + 1), and boil gently for a few minutes to dissolve any dehydrated ferric or aluminum sulfate. (The solution should be clear.) Rinse into a beaker, make to a volume of about 150 cc. with hot water, and precipitate the iron and aluminum as phosphates either by adding ammonia to neutrality, using methyl orange as an indicator, or by making the solution just alkaline with ammonia, just clearing with hydrochloric acid, and then adding 25 cc. of ammonium acetate solution, sp. gr. 1.04. Filter and wash the precipitate of iron and aluminum phosphates with a boiling hot 2.5 per cent ammonium nitrate solution. Ignite and weigh; fuse the ignited precipitate in a platinum crucible with potassium bisulfate, dissolve the fused mass in dilute sulfuric acid (1 + 1), reduce with pure zinc, titrate the iron with standard permanganate, and calculate the percentage of iron phosphate. From the combined percentage of iron and aluminum phosphates deduct the percentage of iron phosphate, leaving the percentage of aluminum phosphate.

Iron and Aluminum (Molybdate Method).—The procedure for estimating iron and aluminum after removing phosphoric acid (P_2O_5) with molybdic solution, as described for plant ashes, has been used successfully in the analysis of phosphate rock.

Magnesium.—Evaporate the filtrate from the iron and aluminum phosphate to dryness and ignite the residue to expel ammonium salts. Dissolve the residue in 5 cc. of hydrochloric acid (1 + 1), filter, and wash thoroughly. Add ammonia to the filtrate in a slight excess and precipitate magnesium with sodium phosphate as in the analysis of liming materials.

Chromium.¹—Fuse 5 grams of the rock phosphate over the blast with 20 grams of sodium carbonate and 3 grams of sodium nitrate. Thoroughly disintegrate the melt in water, to which a drop or two of methyl or ethyl alcohol has been added to reduce and precipitate the manganese; filter; nearly neutralize the filtrate with nitric acid, having previously ascertained the amount to be used on a blank test with 20 grams of sodium carbonate, etc.; and evaporate the solution to approximate dry-

¹ Hillebrand, U. S. Geol. Survey Bull. 700 (1919).

ness, precipitating the silica and alumina. Dilute with 100 cc. of water, warm, filter, and wash. To obtain any chromium retained by the precipitate evaporate it with hydrofluoric and sulfuric acids, fuse the residue with a little sodium carbonate, nearly neutralize the aqueous extract with nitric acid, boil a few moments, and unite the filtrate with the main one. Add mercurous nitrate to the cold alkaline solution in quantity sufficient to obtain a precipitate of considerable bulk, heat, filter, dry the precipitate, and ignite at not over 500° C. in a platinum crucible after removing the paper to prevent reduction and injury to the crucible. Fuse the residue with a very little sodium carbonate, wash with water, and filter the solution, if colored yellow, into a 25 cc. graduated flask. Determine the chromium by comparing with a standard alkaline solution of potassium monochromate made by dissolving 0.25525 gram of pure potassium monochromate in 1 liter of water made alkaline by a little sodium carbonate.

Vanadium.¹—Add sulfuric acid in slight excess to the solution used for the chromium determination, saturate with hydrogen sulfide, and filter. Boil the filtrate to expel hydrogen sulfide and titrate at a temperature of 70°—80° C. with a dilute solution of potassium permanganate, representing about 1 mg. of V_2O_5 per cubic centimeter, as calculated from the iron strength of the permanganate, one molecule of V_2O_5 being indicated for each one of Fe_2O_3 . Always check by reducing again with sulfur dioxide, boiling to expel excess sulfur dioxide and repeating the titration. Take the latter result, which is apt to be a little lower than the first, as the correct result.

Silica.—The methods usually employed for the determination of silica are not applicable to the analysis of rock phosphate, owing to loss of silica as silicon fluoride when the sample is digested with acid. The following method² is adapted to the determination of silica in rock phosphate³ and other materials containing fluoride:

Fuse 1 gram of the sample with 6 grams of Na_2CO_3 , leach the cooled melt with hot water, and filter when disintegration of the melt is complete. Transfer the insoluble residue back into the dish by the use of a jet of water, add 100 ml. of a 1 per cent solution of sodium carbonate, boil for a few minutes, filter, and wash thoroughly with hot water. Reserve the residue (*A*) for the determination of silicon dioxide. To the combined filtrates, which should have a volume of approximately 300 ml., add 1 gram of zinc oxide dissolved in 20 ml. of dilute nitric acid, boil for 1 minute, filter, and wash the residue thoroughly with hot water. Reserve the precipitate (*B*) for the determination of silicon dioxide. Add a few drops of methyl red to the filtrate, nearly neutralize with nitric acid, and evaporate to a volume of 200 ml., being careful that the solution remains alkaline during the evaporation. Finish the neutralization of the concentrated solution with nitric acid until the color is a delicate pink. Now add 1 gram of zinc oxide dissolved in ammonium

¹ Hillebrand, U. S. Geol. Survey Bull. **700** (1919).

² Hoffman and Lundell, U. S. Dept. Commerce Research Paper No. 110.

³ Hill and Jacob, *J. Assoc. Official Agr. Chem.*, **13**, 112 (1930).

hydroxide + ammonium carbonate, and boil until the odor of ammonia is entirely gone. This usually requires boiling until the volume of the solution has decreased to about 50 ml. After all the ammonia is expelled, add about 100 ml. of warm water, stir, allow to stand for a few minutes, filter, and wash the precipitate (C) with cold water. The filtrate contains the fluorine.

With the aid of a jet of dilute hydrochloric acid (1 + 20), transfer the insoluble residue (A) and the two zinc precipitates (B and C) from the papers to the dish in which the latter precipitation was made. Ignite all papers used in the preceding filtrations and add any residue so obtained to the contents of the dish. Now add 25 ml. of concentrated hydrochloric acid and determine silicon dioxide by a second dehydration and intervening filtration in the usual manner.

To recover the silicon dioxide left in the filtrate, after the second dehydration, add about 0.05 gram of aluminum oxide (in the form of aluminum chloride) and 10 grams of ammonium chloride, and precipitate the aluminum with ammonium hydroxide. Dissolve the precipitated hydroxide in 50 ml. of dilute sulfuric acid (1 + 10), dehydrate, filter, and add the small quantity of silicon dioxide to that obtained above.

Carbon Dioxide, CO_2 .—Proceed as directed for carbon dioxide under the analysis of liming materials.

Fluorine.—Fluorine is a normal constituent of rock phosphate. Samples from different deposits vary considerably in their fluorine content, the average for commercial types of rock mined in the United States being about 3.5 per cent. The more recent island deposits, which show considerable organic matter, contain less fluorine than the mineral deposits of rock phosphate.

Fluorine fumes evolved from the treatment of rock phosphate with sulfuric acid in the manufacture of superphosphates were formerly of considerable annoyance and discomfort to the workmen. However, at the present time factories are equipped with apparatus for recovering the hydrofluoric acid fumes and converting them into a useful by-product, fluosilicate, which is being used as an insecticide. An accurate method for the determination of fluorine is of practical importance to the manufacturer of superphosphate in the recovery of the fluorine fumes as a by-product, and such a method is also of importance to the manufacturer of phosphates used for food and mineral mixtures in feed for live stock.

METHOD FOR THE DETERMINATION OF FLUORINE IN PHOSPHATE ROCK AND SIMILAR MATERIALS¹

REAGENTS

(1) *98.5 per cent sulfuric acid.*—This is most conveniently prepared by adding sufficient fuming sulfuric acid to ordinary concentrated sulfuric acid to give a solu-

¹ Reynolds, Ross and Jacob, *J. Assoc. Official Agr. Chem.*, **11**, 225 (1928).

tion containing about 99 per cent sulfuric acid. The solution is heated in a large beaker, preferably on a hot plate, for about 1 hour after it begins to fume strongly, in order to remove free sulfur trioxide and sulfur dioxide. (The latter appears to be present in appreciable quantity in some samples of sulfuric acid prepared in the above manner.) If the final product contains more than 98.5 per cent of sulfuric acid, dilute with the correct quantity of 95 per cent acid, or if it contains less than 98 per cent sulfuric acid, more fuming acid is added. In either case, the acid as finally used should contain 98–98.5 per cent sulfuric acid, as determined by titration with standard alkali.

(2) *Silver sulfate*.—A 10 per cent solution of silver sulfate in 98–98.5 per cent sulfuric acid is prepared and heated until it fumes strongly in order to remove volatile impurities. Certain samples of supposedly C. P. silver sulfate have been found to contain considerable nitrate. This solution is used to absorb the hydrogen chloride that is evolved when chlorides are present in the sample.

(3) *Chromium trioxide*.—The pure material is dried at 105°–110° C. and finely ground. A suspension, containing preferably a large excess of solid chromium trioxide, is made in 98–98.5 per cent sulfuric acid. This reagent is used to absorb sulfur dioxide, nitric acid, and oxides of nitrogen.

(4) *Silica*.—The commercial grade of quartz flour is satisfactory. It should be ground to 200 mesh and ignited at a low red heat to remove organic matter and moisture. Samples of quartz flour have been found to contain as high as 0.06 per cent of fluorine. Any fluorine present can be removed by digesting the material with sulfuric acid, preferably about 98 per cent strength, at temperatures of 250°–300° C.

(5) *Standard alkali and acid*.—Tenth-normal solutions of sodium hydroxide and hydrochloric acid are prepared. One cubic centimeter of 0.1 *N* sodium hydroxide is equivalent to 0.0019 gram of fluorine.

APPARATUS

The apparatus required for the determination is assembled as shown in Fig. 4 and is composed of the following individual pieces:

(1) A gas-washing bottle, *A*, containing concentrated sulfuric acid for removal of moisture from the inlet air.

(2) A cylinder, *B*, loosely packed with glass wool and phosphorus pentoxide, also for moisture removal.

(3) A reaction flask, *C*, for digesting the sample with 98–98.5 per cent sulfuric acid. The flask, shown in detail in Fig. 5, is made of Pyrex glass and is designed especially for this purpose. It is composed of a principal tube, *c*, having an opening, *d*, for introducing the sample and acid. Dry air is drawn into the tube through *a* and the gaseous reaction products pass out through the bulbed tube, *e*. The porcelain plate, *b*, about 2.5 cm. in diameter and having perforations about 0.3 mm. in diameter, makes close contact with the walls of the tube, *c*, and is held in place by indentations in the glass above and below the plate. It serves to prevent portions of the sample from being carried up into the air-inlet tube, *a*, when the acid is added, and at the same time it permits free passage of air through the acid during digestion.

(4) A furnace, *D*, with rheostat, *E* (not shown), for heating the reaction tube. A type 84, multiple unit, electric crucible furnace is satisfactory and convenient for

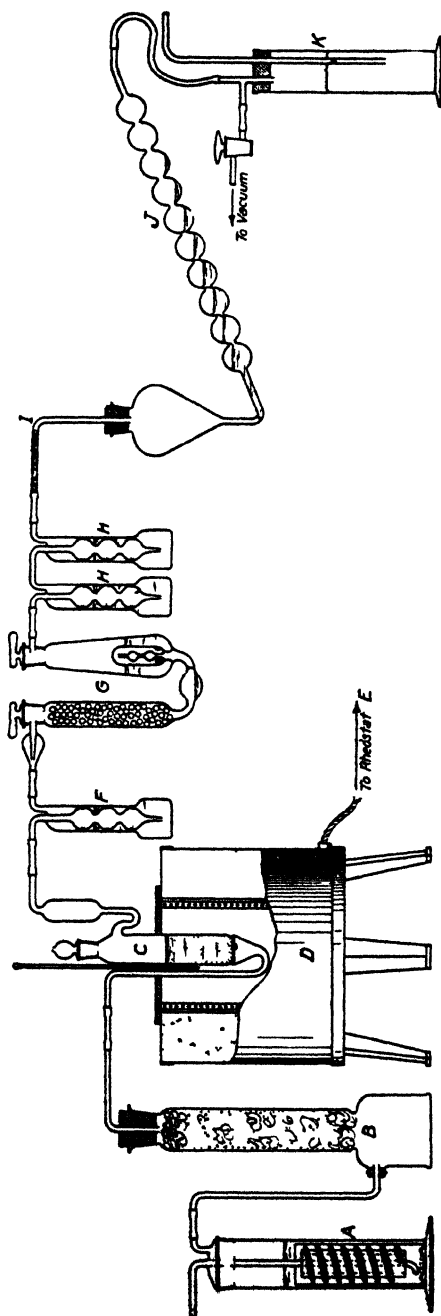


FIG. 4.—Apparatus for the Determination of Fluorine in Phosphates

this purpose. A suitable electric furnace may be made by winding the proper quantity of nickel-chromium wire on a porcelain, alundum, or fire-clay core of the proper size. The reaction flask should be placed in the furnace so that the level of the sulfuric acid is below the top of the furnace, which is covered with a piece of asbestos board containing openings for the tube and thermometer.

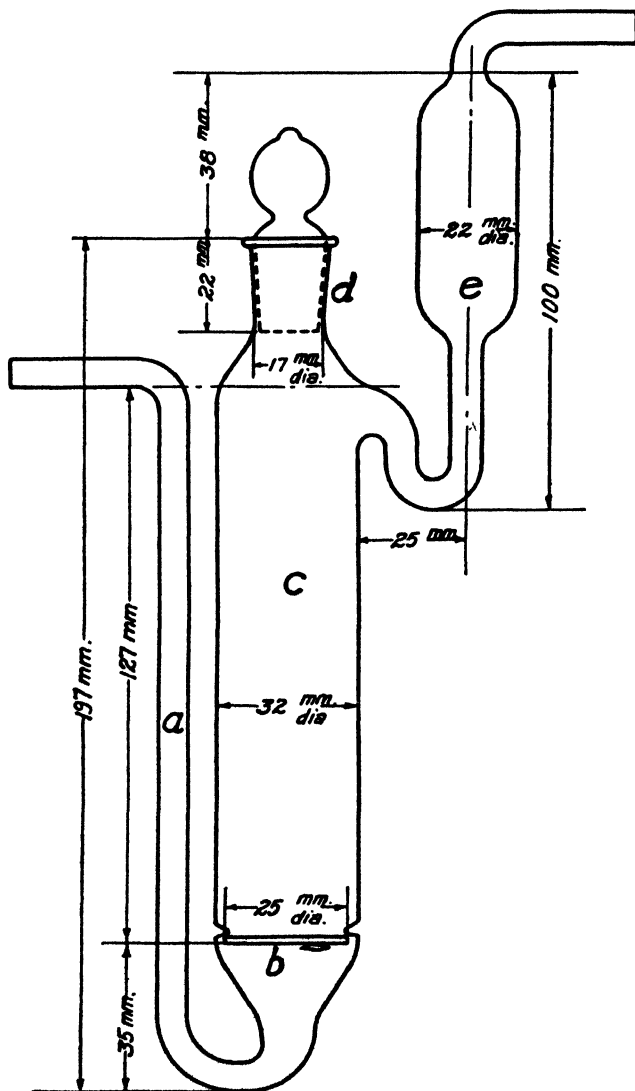


FIG. 5.—Reaction Flask Used in the Determination of Fluorine in Phosphates.

(5) A Bowen potash tube, *F*, containing 98–98.5 per cent sulfuric acid.

(6) A Schmitz sulfuric acid tube, *G*, containing the 10 per cent solution of silver sulfate in 98–98.5 per cent sulfuric acid. The cylindrical arm of this tube is filled with glass beads moistened with the silver sulfate solution.

(7) Two Bowen potash tubes, *H*, having the exit end of the first tube fused to the inlet end of the second. Both tubes contain the suspension of chromium trioxide in 98–98.5 per cent sulfuric acid. The contents of the tubes are renewed when most of the chromium trioxide has been removed from suspension.

(8) A glass tube, *I*, filled with glass wool. This tube is approximately 0.5 cm. in diameter and is bent at right angles about 16 cm. from the inlet end. Wagner and Ross have pointed out that it is necessary to pass the reaction gases through a tube filled with glass wool in order to remove sulfur trioxide efficiently. Care should be taken to replace the tube before the glass wool becomes completely saturated, as indicated by a perceptible coloration of the wool when it is heated to 100°–130° C.

(9) A Meyer sulfur tube, *J*, containing 50 cc. of distilled water and 10 cc. of 0.1 *N* hydrochloric acid and connected with the tube *I*, by means of a rubber stopper. The exit end of the Meyer tube is connected with a source of vacuum through a pressure-regulating vessel, *K*, containing mercury.

All connections, except the one between the two Bowen tubes, *H*, are made of rubber, and the permanent rubber connections are coated with shellac. The ground-glass stopper in the reaction flask *C* is lubricated with 98–98.5 per cent sulfuric acid. The other ground-glass stoppers are lubricated either with sulfuric acid or a good grade of stopcock grease. When the apparatus is not in use, all openings are closed to prevent absorption of moisture from the air by the sulfuric acid solutions.

PROCEDURE

The sample for analysis is ground to pass a 200-mesh sieve. Its weight will depend on the fluorine content of the material, but a maximum sample of 1 gram, equivalent to about 30–40 mg. of fluorine, is preferable in the analysis of phosphate rock. The sample must be thoroughly dry, and if it contains an appreciable quantity of organic matter, as is frequently the case with phosphate rock, it should be intimately mixed in an agate mortar with about 0.5 gram of calcium oxide and ignited in a muffle furnace at 500°–600° C. for 2 hours.

The prepared sample is thoroughly mixed with 200-mesh silica in an agate mortar and transferred to the dry digestion flask. Addition of anhydrous copper sulfate to prevent bumping, as recommended by Wagner and Ross, is not necessary when the tube is heated in an electric furnace and the reaction mixture is agitated by a current of air. If the sample does not exceed 0.5 gram, 0.5 gram of silica will be sufficient, but with larger samples a quantity of silica equal to the weight of the sample should be used. The digestion tube is connected in place in the furnace, and 40 cc. of 98–98.5 per cent sulfuric acid is added. If the sample contains considerable carbonate, the acid may be added slowly from a dropping funnel connected with the digestion flask through a rubber stopper, while a slow current of air is drawn through the apparatus. When all the acid has been added, the funnel and rubber stopper are quickly replaced by the ground-glass stopper. Most of the carbonate also may be removed, prior to digestion with sulfuric acid, by mixing

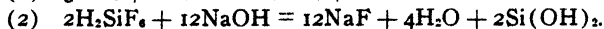
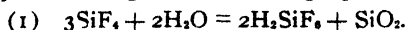
the sample with about 0.5 gram of lime and igniting at 750°–800° C. for 1 hour, loss of fluorine being negligible in most cases.

After the addition of the acid, air is drawn through the apparatus at such a rate that a continuous stream of bubbles is obtained. The temperature of the digestion tube is rapidly raised to about 250° C. and then slowly increased to about 300° C. in the course of about 45 minutes. The temperature is determined by means of a thermometer placed with the bulb against the wall of the digestion flask at a point about halfway up the sulfuric acid column. After the tube has been heated for about 15 minutes, it is shaken at frequent intervals to facilitate solution of the white scum that forms on the surface of the acid. The presence of fluorine is characterized by the formation of this white scum. Digestion of the sample, continued until the scum disappears, usually requires about 1 hour. Heating is then discontinued, and aeration is continued 15–20 minutes longer.

The Meyer sulfur tube is then disconnected, and its contents are transferred to a 500 cc. flask. The silica deposited in the tube is removed as completely as possible, and the tube is rinsed several times with distilled water. The final volume of solution and rinsings in the flask is made up to 200–250 cc. Ten cubic centimeters of the standard hydrochloric acid is placed in another flask of the same size and diluted to the same volume. The contents of both flasks are heated to boiling under as nearly the same conditions as possible—an electric hot plate gives very uniform results—and the boiling is continued for 5 minutes to remove carbon dioxide and as much sulfur dioxide as possible. The contents of both flasks are titrated hot with 0.1 *N* sodium hydroxide, phenolphthalein being used as an indicator. The end point is usually fairly sharp, and it should be approached carefully.

The final results can be corrected for the small quantity of sulfite and sulfate that is usually present in the titrated solution with sufficient accuracy, in most cases, by adding bromine water to oxidize the sulfite to sulfate. The solution is allowed to stand overnight, and the milky solution obtained by adding 10 per cent barium chloride solution acidified with hydrochloric acid is compared with solutions containing 0.05–0.3 cc. of 0.1 *N* sulfuric acid in the same volume of water. The small quantity of silica present is usually in such a granular condition that it does not interfere with the test. The total sulfate found in samples containing but little organic matter should not exceed the equivalent of 0.2 cc. of 0.1 *N* sulfuric acid and is usually much less than this figure.

From the total sodium hydroxide titration there should be subtracted the equivalent of the fluorine blank on the reagents, the equivalent of the hydrochloric acid used in the absorption tube, and the equivalent of the sulfate found in the titrated solution to obtain the net sodium hydroxide equivalent of the fluorine content of the sample according to the following equations:



The hydrated silica does not react with the dilute standard alkali solution. The purpose of the hydrochloric acid in the Meyer tube is to decrease the tendency of sulfur dioxide to oxidize to sulfur trioxide, but it is questionable whether there is any advantage in its use if the quantity of

organic matter in the sample is small. Dilute solutions of hydrofluosilicic acid do not lose fluorine when boiled for a short time.

The authors state that the procedure outlined has been used for the determination of fluorine in approximately 100 samples of different grades of phosphate rock from domestic and foreign deposits. No difficulty was experienced in obtaining duplicate results that agreed within 0.1 per cent and usually to within less than 0.05 per cent of fluorine.

Recovery of 92-94 per cent of the fluorine present in pure calcium fluoride was obtained by digesting the sample with 98-98.5 per cent sulfuric acid for 1 hour at 300° C. The presence of calcium, iron, and aluminum phosphates and sodium arsenate did not interfere in the recovery of fluorine from pure calcium fluoride, but boron in the form of borax had a detrimental effect. Addition of lime prevented loss of fluorine when samples of phosphate rock were ignited at temperatures up to 750° C. in order to remove organic matter.

Iodine.—The presence of iodine has been detected in many natural phosphates and is of interest in the discussion of the theory of their origin.¹ A qualitative test for the detection of iodine may be applied in the following manner: A few grams of finely ground phosphate is mixed with strong sulfuric acid, and the gases arising from the reaction are aspirated into a small quantity of carbon disulfide or chloroform. The violet coloration arising indicates the presence of iodine. The gases carrying the iodine may also be brought into contact with starch paste, the well-known blue color being produced. The quantity of iodine present in a phosphate is rarely more than 0.001 per cent.

*Iodine in Phosphate Rock High in Carbonates.*²—Bring the finely powdered material to a thick paste by stirring with a strong caustic soda solution in an iron dish. Completely dry, pulverize the residue, and ignite strongly for about 30 minutes over a blast, keeping thoroughly stirred so as to effect complete combustion of the organic matter that is practically always present in natural phosphates. Continue to stir while heating. Digest the product of the ignition with hot water several hours in a spacious porcelain dish, filter and wash the residue several times with hot water. If the filtrate has a yellowish to brownish color, indicating unoxidized organic matter, evaporate it to dryness and ignite again with stirring. Unite the filtrate and washings either at once or after a preliminary concentration. Neutralize with 20 per cent sulfuric acid at room temperature, taking care to avoid losses due to the vigorous evolution of carbon dioxide. Concentrate the solution further, seeing that it does not acquire an acid reaction, add concentrated ammonia to precipitate

¹ L'Engra's, 10, 65 (1895).

² Wilke, Druett, Beck and Phipp, *Z. anorg. allgem. Chem.*, 172, 344 (1928).

silica and iron and aluminum hydroxides, etc., filter and wash. Evaporate the filtrate and wash waters, stirring constantly (best with a mechanical stirrer) and adding occasionally some concentrated ammonia to avoid an acid reaction, until the greater portion of the foreign salts, chiefly sodium sulfate, has separated, preferably until the filtrate from the crystals is not more than 30-50 cc. Filter, wash several times with a little hot water, and again concentrate the filtrate and wash water to 30-50 cc. and place in a 250 cc. separatory funnel. Measure accurately into the separatory funnel 1 cc. of chloroform for each 200-300 micrograms¹ of iodine ex-

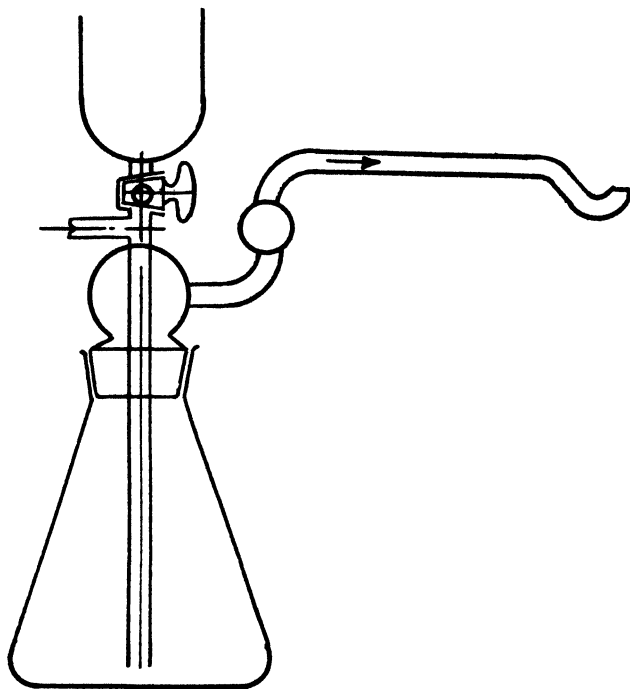


FIG. 6.—Decomposition Flask for Iodine Determinations.

pected and add a few cubic centimeters of nitrous acid. Shake so that the liberated iodine is taken up by the chloroform. When the chloroform has settled, measure 0.05-0.1 cc. of it into an iodine comparison tube,² cover with 1 cc. of extracted liquid from the separatory funnel, and compare the color with known standards in similar tubes.

*Iodine in Phosphate Rock Low in Carbonates.*³—Add dropwise enough water to 20-100 grams of very finely ground material, in a dry decomposition flask (Fig. 6),

¹ One microgram (γ) = 0.000,001 gram = 0.001 mg.

² Th. v. Fallenberg, *Biochem. Z.*, **139**, 396 (1923).

³ Wilke-Dörfurt, Beck and Plepp, *Z. anorg. allgem. Chem.*, **172**, 344-52 (1928).

to moisten it thoroughly. Connect the flask with a wash bottle through which carbon dioxide or nitrogen is passed and with a three-bulbed receiver tube and wash bottle, each containing a sodium hydroxide solution. When a moderate flow of gas has been established through the apparatus, carefully run 1-2 cc. of concentrated sulfuric acid into the flask. Adjust the rate of addition of more acid according to the gases evolved, stopping when the evolution ceases. Now heat the flask in an oil bath gradually to 220°-230° C. for 3 hours to insure that all volatile substances are carried by the gas stream into the receiver. Wash the contents of the receiver into a beaker, wash the receiver and the connecting tube with hot dilute sodium hydroxide solution, neutralize the united liquors carefully, add ammonia, filter if necessary, evaporate to 30-50 cc., and complete the determination as directed above.

BASIC SLAG

Calcium.—Treat 5 grams of the finely ground sample in a 250 cc. porcelain dish with 25 cc. of hydrochloric acid (1 + 1) and 5 cc. of nitric acid (1 + 1), stirring and digesting on a hot water bath until the contents of the dish acquire a gelatinous consistency. Evaporate the contents to dryness and bake on a sand bath at about 120° C. until the hydrochloric acid is expelled. Moisten the dry residue with 10 cc. of hydrochloric acid (1 + 1), digest for 5 minutes on the hot water bath, dilute with hot water, and further digest for 10 minutes, stirring thoroughly. Filter out the silica and wash thoroughly. Transfer the filtrate into a 200 cc. volumetric flask, cool, make to the mark, and mix. Determine total calcium in a 10 cc. aliquot by the method described for the determination of total calcium in rock phosphate. The calcium in basic slag occurs in combination with phosphorus and silica, also as free lime; a small amount occurs as carbonate, which is probably the result of air slaking of the lime after the grinding of the slag.

Manganese.—Weigh 5 grams of the finely powdered basic slag into a 250 cc. porcelain dish, add 10 cc. of strong hydrochloric acid, cover the dish with a watch-glass, and digest on a water bath for 30 minutes. Rinse the watch-glass into the dish, evaporate to dryness, and heat on a sand bath until all odor of hydrochloric acid is evolved. Moisten the dry residue with hydrochloric acid (1 + 1) and 50 cc. of hot water, digest for 15 minutes on the water bath, filter out the silica, and thoroughly wash with hot water. Transfer the filtrate to a 100 cc. volumetric flask, cool, dilute to the mark, and mix. Transfer a 10 cc. aliquot to a 100 cc. porcelain dish on a water bath, add 10 cc. of sulfuric acid (1 + 1), and heat on the water bath until the odor of hydrochloric acid is expelled. Transfer the solution to a 100 cc. Erlenmeyer flask, add 0.01 gram of potassium periodate, and heat until the purple color of permanganic acid develops. Transfer to the water bath and heat for an hour; cool, make the solution to a definite volume, mix, and determine manganese according to the colorimetric periodate method as described for manganese in liming materials.

BONE MEAL

Calcium.—Ignite 10 grams of the sample to destroy organic matter, transfer to a beaker, and proceed as directed for the determination of calcium in rock phosphate.

Fat.—Weigh 2 grams of finely ground bone meal and extract with ether as directed in the chapter on Meat and Meat Products, *Methods of Analysis, A. O. A. C.*

Fineness.—Weigh 100 grams of the material and transfer it onto a sieve having circular openings 1/50 inch (0.5 mm.) in diameter. Sift, breaking any lumps with a rubber pestle. Weigh the portion that remains on the sieve and determine the fine portion that passed through the sieve by difference. The degree of fineness guaranteed by the manufacturer of basic slag is 90 per cent to pass through a 100-mesh sieve.

V.—MISCELLANEOUS CONSTITUENTS OF NITROGENOUS FERTILIZERS

Calcium Cyanamide, Cyanamide, Nitrolime, CaCN_2 .—This compound is formed by heating calcium carbide to a temperature of about 1100°C . and passing a stream of nitrogen gas through the hot material. The nitrogen combines with the calcium carbide to form calcium cyanamide according to the equation $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$. The nitrogen gas must be pure and nitrification of the carbide must be continued to completion, otherwise undesirable compounds will be formed with the calcium carbide. The finished product found on the market shows considerable variation in composition. For example, analyses reported from three different sources give the following results:

RESULTS OF ANALYSES OF CALCIUM CYANAMIDE.

	No 1	No 2	No. 3
	Per cent	Per cent	Per cent
Moisture (H_2O)	—	—	3.47
Calcium cyanamide (CaCN_2)	58.91	29.26	45.92
Calcium oxide (CaO)	23.55	—	—
Calcium sulfide (CaS)	—	—	1.73
Calcium carbonate (CaCO_3)	—	0.21	4.04
Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$)	—	20.06	—
Calcium hydrate ($\text{Ca}(\text{OH})_2$)	—	28.78	26.60
Sodium cyanamide (Na_2CN_2)	—	10.38	—
Magnesium oxide (MgO)	.05	—	0.15
Iron and aluminum oxides (Fe_2O_3 and Al_2O_3)	2.44	2.06	1.98
Silica (SiO_2)	2.19	1.03	1.62
Carbon (C)	12.86	7.89	13.14
Total	100.00	99.67	98.65

Cyanamide finds its principal use in agriculture as a source of nitrogen for plants. When it is applied to the soil it absorbs moisture and undergoes changes not fully understood. However, the final products are calcium nitrate and calcium carbonate.

Assuming that all the nitrogen of cyanamide is converted to nitric acid, which combines with calcium to form calcium nitrate, there will still be

an excess of calcium to form carbonate, and the use of calcium cyanamide will tend to maintain neutrality in the soil.

According to Pranke¹ cyanamide manufactured in America since 1912 does not contain any nitrates and the Kjeldahl or Gunning method may be used for the determination of total nitrogen in the compound.

Sodium Nitrate, Chile Saltpeter, NaNO_3 .—The commercial product contains small quantities of potassium, calcium, magnesium, phosphorus, sulfates, chlorides, chlorates, perchlorates, iodides and iodates. Since the quantity of any one of these constituents is small, it is not always necessary to resort to quantitative determinations. However, if it should be desirable to make determinations of chlorides, chlorates, perchlorates and iodides in Chile saltpeter, the methods given on pp. 463-4 are applicable.

Poultry Manure.—The quantity of poultry manure produced on the farm has been estimated to be about 30 pounds per bird annually. Since this kind of manure is rich in nitrogen and mineral matter, unusual care should be taken to conserve and utilize it in the most economical manner possible. To prevent the loss of nitrogen the fresh moist material should be mixed with a dry absorbent such as land plaster (gypsum), shattered leaves of plants or cut straw, and stored in a dry place until it is ready for use. The manure of hens fed ground oystershell or limestone will contain considerable calcium, and therefore its use adds to the soil a certain amount of this element as well as appreciable quantities of phosphorus and potassium. Undoubtedly it is the correct proportions and the easily available form of the nitrogen, phosphorus, calcium and potassium in this kind of manure that make it a favorite among truck gardeners.

Guano and Cave Deposits.—The principal constituents of value in these deposits are nitrogen and phosphoric acid. The other organic matters are also of some value, but they have no commercial rating. The nitrogen may be present in all its forms, *vis.*, organic, ammoniacal, amide, and nitric, and for this reason it is well suited to furnish nourishment to the plant in the earlier stages of its growth as well as to supply its later needs. In caves, due usually to the presence of bats, similar forms of fertilizers are found, and the soluble constituents due to decay and nitrification are protected from the leaching to which they would be subjected in the open air.

In some localities in the United States a few open deposits are found, but the humidity of the climate, except in the arid regions of the West, has prevented the formation of the immense open deposits of guano that

¹ Cyanamid (1913).

characterize some of the arid islands of the Pacific Ocean. In old cave deposits the processes of decay and nitrification seem to have been completed, and very little power of inducing nitrification in culture solutions seeded from these samples has been found.

Waste Leather.—This material belongs to that class of nitrogenous substances which have a small immediate value for plant nutrition. The chief manurial value is found in its nitrogen content. Its value as available plant food has been investigated by Lindsey,¹ who also gives a complete resumé of the literature.

A satisfactory way of identifying leather waste is by the process proposed by Dabney.² It depends on the color produced in a solution of iron phosphate by the tannin compounds derived from the leather. The reagent is prepared by dissolving a freshly made precipitate of iron phosphate from 10 grams of ferric chloride in 400 cc. of an aqueous solution of 40 grams of glacial phosphoric acid. A gentle heat promotes the solution of the phosphate.

In the case of a fertilizer supposed to contain leather, about 1 gram of the material is treated with 30 cc. of water and a few drops of sulfuric acid. The mixture is boiled and poured on a filter. To a portion of the filtrate, some of the solution of iron phosphate is added and the mixture is made alkaline with ammonia. If leather is present in the sample, a purple or wine color will develop. By this method leather can be detected when it is added in 10 per cent quantities. Lindsey regards this method as superior to the microscopic method, which is unreliable in the case of finely ground material.

Hair and Horn.—Waste hair and horn also have a high nitrogen content, and in certain circumstances they may become valuable for manurial purposes. To this end, however, a treatment similar to that prescribed for leather is imperative. In the natural state hair and horn decay so slowly as to be of little practical use for plant food, but the preliminary digestion of these substances with sulfuric acid brings a large proportion of their nitrogen within reach of the growing crop.

Fertilizer materials sometimes contain adulterants such as sand, sawdust, ashes, powdered coal, gypsum, etc. Samples should therefore be subjected to a careful examination, to see if adulterants are present.

¹ *J. Agr. Sci.*, 8, 49, 98 (1894).

² North Carolina Agr. Exp. Sta. Bull. 3 (1879).

DETERMINATION OF MISCELLANEOUS CONSTITUENTS OF NITROGENOUS FERTILIZERS

CALCIUM CYANAMIDE

Dicyandiamide.—According to Pranke,¹ of the various methods for the determination of dicyandiamide in cyanamide that of Caro¹ seems to be the best. The method is as follows:

REAGENTS

(a) *Silver acetate solution.*—Place 100 grams of silver acetate in a liter flask, cover with 400 cc. of 10 per cent ammonium hydroxide, fill the flask to the mark with water, and mix

(b) *10 per cent solution of potassium hydroxide.*

DETERMINATION

Agitate 5 grams of cyanamide with 450 cc. of water for about 2½ hours and fill the flask to 500 cc. Treat an aliquot of 250 cc. with ammonia until it smells strongly thereof and then with silver acetate solution in excess. After shaking and allowing to stand a short period, filter the precipitate of silver cyanamide salts until free of ammonium salts and determine nitrogen in the precipitate by the Kjeldahl method. Then treat an aliquot part of the filtrate, which is now free of cyanamide, with an excess of potassium hydroxide solution and boil until the ammonia is expelled. The precipitate contains all the dicyanamide and some silver oxide. Dilute the solution with an equal volume of water, filter and wash the precipitate, and determine its nitrogen content by the Kjeldahl method.

Calcium and Magnesium.—Weigh and transfer 0.5 gram to a beaker and digest in 20 cc. of hydrochloric acid (1 + 1), stirring occasionally for 15 minutes. Filter out and wash the insoluble residue and determine the calcium and magnesium in the filtrate according to the method for these elements given under the analysis of limestones.

SODIUM NITRATE

Total Chlorine.—Fuse 5 grams of the sodium nitrate in a platinum dish with three times its weight of calcium hydrate or sodium or potassium carbonate, whereby all of the chlorine compounds are converted to chlorides. If the compounds are present as alkali salts, fuse with ammonium chloride in a platinum dish and determine the total chlorides in an aliquot after dissolving the residue in nitric acid and making the solution to a definite volume.

Chlorate.—Weigh 5 grams of the sodium nitrate and transfer to a 250 cc. Erlenmeyer flask; add 150 cc. of 1 per cent acetic acid and 10 grams of zinc dust (Cl-free), and boil for 30 minutes. Filter, wash, and determine chlorides by acidifying the solution with nitric acid (cold) and precipitating with silver nitrate; filter, wash, dry and weigh the silver chloride. Subtract the weight of silver chloride

¹ Cyanamid, p. 20 (1913).

obtained under "chloride" to give the weight of silver chloride corresponding to the chlorate.

Chloride.—Weigh 5 grams of the sodium nitrate and transfer to a 150 cc. Erlenmeyer flask; dissolve the salt in cold water, acidify with cold nitric acid, filter, and wash any insoluble residue. Precipitate chlorides by the addition of silver nitrate, filter, wash, dry, and weigh the silver chloride.

Perchlorate.—Subtract the weight of silver chloride obtained under "chlorate" from the weight of silver chloride under total chlorine and multiply the difference by the factor for the perchlorate.

The factors are as follows:

$\text{AgCl} \times 0.2474 = \text{Cl}$	$\text{Cl} \times 3.4563 = \text{KClO}_3$
$\text{AgCl} \times 0.4078 = \text{NaCl}$	$\text{Cl} \times 3.9075 = \text{KClO}_3$
$\text{AgCl} \times 0.5202 = \text{KCl}$	$\text{Cl} \times 2.1027 = \text{KCl}$
$\text{AgCl} \times 0.8550 = \text{KClO}_3$	$\text{Cl} \times 3.0028 = \text{NaClO}_3$
$\text{AgCl} \times 0.9667 = \text{KClO}_3$	$\text{Cl} \times 3.4535 = \text{NaClO}_3$

Iodine.—Weigh 10 grams of the pulverized salt, transfer to a beaker, and extract the iodides and iodates by digesting and stirring with strong alcohol. Decant the alcoholic extracts through a filter, add a few drops of 10 per cent sodium hydroxide, and evaporate to dryness on the hot water bath. Dissolve the residue in a few cubic centimeters of water and determine the iodine according to the method described for iodine in phosphatic fertilizers.

GUANO

Oxalic Acid.—Weigh 5 grams of guano into a beaker, add 50 cc. of hot water, digest with stirring for 15 minutes, and filter; wash, make the filtrate alkaline with ammonia, and filter; wash the precipitate, add a solution of calcium chloride in excess to the hot filtrate, and filter; wash the precipitate of calcium oxalate and ignite. Calculate the percentage of oxalic acid

Uric Acid.—Uric acid is a natural constituent of Peruvian guano. If it is necessary to make a quantitative determination of the uric acid in guano the methods of Benedict¹ or Folin² are applicable.

VI.—RARER FERTILIZER ELEMENTS OF STIMULATIVE OR CATALYTIC EFFECT UPON CROP GROWTH

MANGANESE, COPPER, ZINC AND BORON

Recent experiments conducted at the Kentucky Agricultural Experiment Station show that small quantities of manganese, copper, zinc and boron have beneficial effects on the growth of plants. It has also been demonstrated by other investigators that when small quantities of compounds of these elements are added to certain soils in this country a remarkable

¹ *J. Biol. Chem.*, **52**, 387 (1922).

² *Ibid.*, **54**, 153 (1922).

stimulation in the growth of plants occurs. In practical agriculture some depleted soils may require the addition of small quantities of available compounds of manganese, copper, zinc and boron in order to restore and maintain productivity and to produce a food supply containing the vital factors in normal proportion.

Manganese.—Weigh 10 grams of finely ground commercial fertilizer into a silica dish and ignite gently until all organic matter is consumed; cool, and digest on the hot water bath with hydrochloric acid (1 + 1) with stirring; filter out and wash the insoluble residue. Make the filtrate to 100 cc., transfer an aliquot of 50 cc. to an evaporating dish, add 10 cc. of strong sulfuric acid, and heat on the water bath until the hydrochloric acid is expelled. If considerable calcium sulfate is present, filter on an asbestos pad and wash. Transfer the filtrate to a 200 cc. Erlenmeyer flask, add about 0.05 gram of potassium periodate, and boil over a Bunsen flame, rotating the flask in the meantime until the characteristic purplish permanganic acid color develops. Continue to heat on a hot water bath for an hour and set aside to cool. If the color is deep purple, dilute the solution to a definite volume. Remove an aliquot and match against a standard manganese solution in Nessler jars or in a colorimeter. Compute the results as percentages of manganese (Mn or Mn_2O_3). The standard solutions of manganese are prepared as described under manganese in limestone.

Copper.—Weigh 100 grams of the finely ground fertilizer into a beaker and add enough water to cover the fertilizer and 25 cc. of hydrochloric acid (1 + 1). Place the beaker on a hot water bath and digest with occasional stirring. Filter and wash the insoluble residue. Evaporate the filtrate until the hydrochloric acid is expelled. Dissolve the residue in hot distilled water and enough dilute hydrochloric acid to bring the soluble salts into solution with considerable stirring; dilute to about 400 cc. with water and heat to near boiling. Saturate the hot solution with hydrogen sulfide, stopper tightly, and set aside until the precipitate has settled to the bottom of the flask and the solution has cooled to room temperature. Filter and wash any precipitate that has formed with a cold dilute solution of hydrochloric acid (1 + 10) that has been saturated with hydrogen sulfide. Finally, rinse the precipitate of copper sulfide three times with distilled water, dry, ignite the copper sulfide to copper oxide, and proceed from this point as described in the method for the determination of copper in limestones.

Zinc.—Weigh 25 grams of fertilizer and transfer to a beaker; digest on a hot water bath with 25 cc. of hydrochloric acid (1 + 1) with occasional stirring; filter out the insoluble residue and wash thoroughly. From this point follow the description given for the determination of zinc in limestones.

Boron.—*Reagents:* Eighty-five per cent phosphoric acid, 95 per cent methyl alcohol and normal hydrochloric acid. *Apparatus:* Two 200 cc. round-bottom flasks, a Liebig condenser, and a 200 cc. Erlenmeyer receiving flask.

DETERMINATION

Transfer 5 grams of the mixed fertilizer to one of the 200 cc. round-bottom flasks, add 5 cc. of 85 per cent phosphoric acid and 20 cc. of methyl alcohol, and

connect with the condenser. Add 100 cc. of methyl alcohol to the other 200 cc. round-bottom flask, and place it in a water bath. Connect the two flasks by means of rubber tubing and bent glass tubes, one of which extends beneath the alcohol in the flask connected with the condenser. Place the receiving flask in position at the end of the condenser and apply sufficient heat to the water bath to keep a steady flow of bubbles of methyl alcohol vapor passing through the flask directly connected with the condenser. (This flask must be heated sufficiently to keep the volume of liquid in it at about 25 cc.). Distil until 100 cc. of distillate is collected. Add 3 drops of phenolphthalein indicator to the distillate and 0.1 *N* sodium hydroxide to a permanent pink color. Stopper the flask, shake well, connect with a condenser by means of a Hopkins bulb, and distil off the alcohol on a water bath. Transfer the residue, which should not be less than 10 cc., to a platinum or porcelain evaporating dish, using as small a quantity of wash water as possible, and evaporate to dryness on a hot water bath. Ignite below redness, cool, and acidify with a few drops of normal hydrochloric acid. Add 25 cc. of water and warm for about 2 minutes on a hot water bath. Filter into a small flask, thoroughly wash the filter, dilute to about 50-75 cc., attach to an air-cooled reflux condenser, and boil gently for a few minutes to remove carbon dioxide. Add 3 drops of methyl red indicator and then 0.1 *N* sodium hydroxide until the red color just disappears. Add about 1 gram of mannitol or less if but a small amount of boron is present. If boric acid is present, the solution will have a pink color at this point, 0.01 or 0.02 per cent usually being sufficient to give the color if the solution has been carefully neutralized with the sodium hydroxide solution. Add 3 drops of phenolphthalein indicator and titrate the solution with 0.1 *N* sodium hydroxide. A blank should be run with the reagents. One cc. of 0.1 *N* sodium hydroxide solution is equivalent to 0.0062 gram of boric acid, or to 0.00503 gram of anhydrous borax. For a more detailed description of the method see *Methods of Analysis*, A. O. A. C.

PART II

INSECTICIDES

AND

FUNGICIDES

INSECTICIDES AND FUNGICIDES

By C. C. McDONNELL, Sc.D., Insecticide Control, Food and Drug Administration, U. S. Department of Agriculture, with the Collaboration of J. J. T. GRAHAM, M.S., C. M. SMITH, B.S., and E. L. GRIFFIN, Ph.D., Senior Chemists, Food and Drug Administration, U. S. Department of Agriculture

CHAPTER I

INTRODUCTION

Insecticides and fungicides are used in large quantities by agriculturists in all parts of the world, their sale amounting to over 100 million dollars annually in the United States alone. Therefore methods of analysis for their determination are important. Since disinfectants also come within the scope of the Federal Insecticide Act, the methods of analysis of this class of materials are also included.

An insecticide is defined in the Federal Insecticide Act of 1910 as "any substance or mixture of substances intended to be used for preventing, destroying, repelling or mitigating any insects which may infest vegetation, man or other animals, or households, or be present in any environment whatsoever." Hundreds of materials fulfil one or more of these functions, or are claimed to do so, and hence the insecticide chemist is called upon to analyze a great variety of products.

Insecticides may be divided into several classes or groups according to their action on insects. One class, frequently called "stomach poisons," includes those materials which, when ingested by insects, produce death through toxic action in the digestive tract. This group, which is the largest, includes the various compounds of arsenic, compounds of fluorine, borax, hellebore, and phosphorous. Another class comprising those compounds commonly called "contact insecticides," which act directly upon the bodies of the insects with which they come into contact, includes such materials as nicotine solutions and dusts, pyrethrum powder and extracts, sulfur, soap, oil emulsions and larkspur extracts. A third class, fumigants, includes those materials which produce vapors that act upon the insects through the respiratory organs, such as liquid hydrocyanic acid, sodium and potassium cyanides, calcium cyanide, paradichlorobenzene, naphthalene, ethyl acetate, carbon tetrachloride, carbon disulfide, sulfur

dioxide and chloropicrin. There are also many materials which are more or less effective, in the strengths in which they are ordinarily used, in repelling such insects as flies and mosquitoes without actually killing them. This group includes pine oil, chloroform, mineral and coal tar oils, and many essential oils—citronella, wintergreen and others. Finally, there are others that act as attractants to lure the insects to traps or poisoned food. A striking example of this group is geraniol in its action in attracting the Japanese beetle.

A fungicide is defined in the Insecticide Act as “any substance or mixture of substances intended to be used for preventing, destroying, repelling or mitigating any and all fungi that may infest vegetation or be present in any environment whatsoever.” From an agricultural viewpoint the most important fungicides are those used for the control of fungi attacking plants, but since the bacteria are a subdivision of the fungi, disinfectants are also treated in this section.

The fungicides most commonly used on plants are sulfur and its compounds, the compounds of copper, and certain mercury compounds, while those used as germicides and disinfectants include hypochlorites, mercury compounds, phenol and other coal tar products, formaldehyde and sulfur dioxide.

For the sake of brevity, whenever any observation relating to insecticides and fungicides in general is made in this section, the term “insecticide” will be used indiscriminately for any of these classes of products.

Some insecticides are produced from certain plants which contain alkaloids or other poisonous constituents. A product consisting of the ground flowers of the plant known as pyrethrum was used centuries ago to kill certain insects, and this is still one of the most important insecticides. This plant is extensively cultivated in Japan and some other countries for this purpose. Tobacco also is used at times with no preparation other than drying and grinding into powder. Several thousand tons of tobacco stems and refuse from factories engaged in the manufacture of tobacco products are used annually in this way, or for the extraction of nicotine for use as an insecticide. The finely ground root of certain species of hellebore is one of the oldest insecticides. The powdered root of some species of derris has also come into use in recent years.

Other insecticides have been made from industrial waste products. For example, London purple, originally the waste product from the manufacture of certain dyes, consisting essentially of the arsenate and arsenite of calcium, is one of the oldest arsenical insecticides, and it was used in large

quantity at one time. The fluorides and silicofluorides may be considered as by-products in that hydrofluoric acid is obtained only incidentally in the manufacture of phosphate fertilizers. On the other hand, the manufacture of most insecticides is now a specialized industry, and the various insecticides are the direct products of the technical operations employed.

While it might seem the more logical way to treat insecticides and fungicides in groups according to their uses, so much overlapping occurs that the writers decided to make a chemical classification and treat them under the headings *arsenicals*, *copper compounds*, *sulfur compounds*, etc., after some general phases of insecticide analysis, such as sampling, physical examination, and preparation for analysis had been discussed.

CHAPTER II

SAMPLING

The sampling of insecticides for analysis involves the same problem as the sampling of any other product—that of selecting from a quantity of material a comparatively small portion which will be representative of the original in its properties and chemical composition. The great variety of materials used as insecticides and fungicides and the heterogeneity of many of them make the proper sampling of such materials a difficult problem, and no hard and fast rules can be established to cover all cases.

Insecticides and fungicides are shipped in packages of various weights and volumes, practically never in bulk. Household insecticides are usually sold in containers holding from 1 ounce to 1 gallon if liquid, and in cartons holding 1 ounce to 1 pound if solid. The strictly agricultural insecticides and fungicides may be put up in 1-10 pound packages for garden use, and 50-200 pound drums for large scale use; or if liquids, in various sizes up to 50 gallon drums. True gaseous materials are practically never encountered among insecticides. Chlorine, sulfur dioxide and hydrocyanic acid when sold for this purpose are packed in steel cylinders under pressure and are in liquid form.

In general, the square root of the number of packages in a shipment may be considered as a sufficient number from which to take samples. These should be selected at random unless some preliminary test, such as is described later in connection with calcium arsenate, is being applied.

The sampling of shipments made up of small packages presents comparatively little difficulty, it being sufficient to select the requisite number of whole packages. Large packages present greater difficulties, because they must be sampled in place. Four distinct cases present themselves, according to the nature of the material.

(1) *Dry Material in the Form of Powder, Granules, Blocks or Lumps.*—If a solid insecticide is finely powdered, or not too coarsely granular, it may be sampled by means of the usual form of sampling “trier” described on p. 11. The trier should be long enough to reach the full length of the drum or barrel. If the head of the container is not removable, the trier may be inserted through holes bored in the head if the container is of wood, or if of metal by removing the cover or cutting out a piece of the metal. If the material is in blocks or lumps, the only course

available is to empty the contents of the container and select pieces at random from various parts of the pile.

(2) *Miscible Liquids*.—In this case sampling is quite simple, since all that is necessary is to agitate the contents of the container to insure thorough mixing and then to draw off a portion by means of a faucet, siphon or dipper.

(3) *Mixture of Liquid and Solid*.—Products of this type are frequently encountered; they vary from mixtures in which the liquid predominates, to stiff pastes in which the solid predominates. The greatest care is necessary in sampling such materials. The solid deposit must be thoroughly distributed through the liquid, by stirring, shaking or kneading, as the case demands, but the ease with which this distribution is accomplished varies greatly. Especial difficulty is encountered when the containers have stood undisturbed for a long time, when the liquid is viscous, or when the product is a stiff paste. After thoroughly mixing the material, the samples must be drawn as rapidly as possible to prevent any appreciable segregation during the process. Thick pastes can sometimes be sampled with a trier as described under solid material, but this should only be attempted by an experienced sampler who is familiar with the character of the material.

(4) *Materials Consisting of Two (or more) Immiscible Liquids*.—This type of product is quite common since it embraces most oil emulsions. No matter how well mixed an emulsion may have been when packed it is subject to some separating out on standing. A properly made emulsion will mix thoroughly with very little agitation and will separate so slowly that samples may be withdrawn without any special precautions. On the other hand, multilayer liquids will sometimes be encountered which separate so rapidly that it is difficult to get a representative sample. In extreme cases it may be necessary to use a cylindrical sampling tube with a valve at the bottom. The tube, with valve open, is slowly immersed in the material until it reaches the bottom of the container; the valve is then closed; the tube is withdrawn, and the contents are transferred to a bottle or other suitable container.

Importance of Individual Samples.—Owing to the fact that a 100 or 200 pound drum of material is sufficient for the treatment of several acres of crop, and hence may cause great damage if it is of inferior grade, an additional question arises in connection with the sampling. The purchaser is not interested solely in a knowledge of the *average* composition of the shipment; he desires to be reasonably sure that every package is

satisfactory. Hence composite samples should not be taken; and those from each package should be kept separate so that analyses of individual packages may be obtained. In case the analysis shows one or more packages to be unsatisfactory for use, all packages in the shipment, if available, should be examined.

In order to lighten the labor of sampling and analysis in such a case, it is sometimes possible to select by simple preliminary tests the samples that are faulty. For example, calcium arsenate that does not contain considerable free calcium hydroxide generally shows high water-soluble arsenic and is consequently injurious to foliage and unsafe to use. A simple test with an alcohol solution of phenolphthalein will serve to indicate those packages containing little or no free lime, and thus those that are probably defective may be easily selected.

Laboratory Sampling.—The same problems that confront the inspector in picking representative samples from a large shipment of packages also confront the analyst when he comes to separate a small working sample from the larger portion submitted. Powdered insecticides sold under proprietary names may be very heterogeneous, and the analyst should take special care to mix them thoroughly. In general all lumpy materials should be ground reasonably fine before analysis. In certain cases it is practically impossible to grind a sample, as for instance when it consists of sodium hydroxide, and in other cases there may be considerable loss of volatile constituents during the grinding, as in the case of cyanides. In these cases, the only course open to the analyst is to put a large sample into solution and take small portions for analysis by aliquoting. Some samples are subject to deterioration, and they must be preserved in special ways. For example, lime sulfur decomposes under the action of the air, and should be preserved in bottles that are filled entirely to the neck. Several small portions should be thus preserved so that if additional tests are needed a fresh bottle can be opened. Samples containing water, naphthalene, paradichlorobenzene, formaldehyde, nicotine, cyanides, hypochlorites or any other volatile material must be preserved in glass containers, with the stoppers sealed, if the analysis is not to be made promptly.

CHAPTER III

PHYSICAL METHODS FOR EXAMINING INSECTICIDES

(a) **Net Weight.**—Obtaining the net weight of packaged samples ordinarily offers no difficulty, since it is only necessary to weigh the package as received, empty the contents, and reweigh the empty package. If it is necessary to wash the container to remove the last of the contents, it should be dried before it is weighed.

No single type of scale is suitable for all net weight determinations. An ordinary large size laboratory balance suffices for samples whose gross weight does not exceed 5 or 6 pounds; a balance weighing to 0.5 or 1.0 gram will be sufficiently sensitive since an error of as much as one gram in a 1 pound sample will represent a departure of only 0.2 per cent. For samples whose gross weight is 10 pounds or more, a small platform scale with a sensitivity of 1 ounce may be used.

(b) **Net Volume.**—Many samples of insecticides are liquids or suspensions of solids in liquids, and the packages bear a statement of content in terms of volume. The determination of net volume presents greater difficulties than the determination of net weight because the volume of liquids varies with the temperature. Therefore a temperature that represents reasonably close the average room temperature throughout the year should be adopted; 20° C. is suggested for this purpose. This is also the temperature at which most specific gravity determinations of liquids are made.

In the case of mobile liquids, the volume may be determined most simply by pouring the contents of the can into a graduated cylinder and reading the volume directly. The analyst should assure himself that no appreciable quantity of liquid remains in the can. If such a determination shows the product to be above the guaranteed volume, this method is considered sufficient. In case the volume is slightly less than claimed, the weight of the liquid adhering to the can may be determined by first weighing the can and material, washing with a suitable solvent to remove the material, drying, and reweighing. From the weight of the adhering liquid and the specific gravity as determined on the bulk of the liquid, the volume of adhering liquid may be calculated. When the sample to be measured consists of a very viscous liquid, it is always necessary to use the combination weight and specific gravity method just described. In the case of emulsions too thick to flow it is impossible to get more than an approximate measurement. The best procedure is to mark the height of the

material in the original container, completely empty and clean the container, and then measure the volume of water necessary to fill it to the mark representing the original level.

(c) **Specific Gravity.**—The determination of specific gravity is valuable in the examination of original samples, such as lime sulfur, mineral oils, tar oils, etc.; in the examination of constituents separated from samples, such as mineral oil from emulsions, alcoholic distillates, and water obtained by the xylene distillation and Penfield methods; and in measurement of net volume as described previously.

When the quantity of liquid available is sufficient, the simplest instruments to use for the determination of specific gravity are the hydrometer and the Westphal balance. For small quantities of liquids, the various forms of pycnometer will prove useful. The 25 and 10 cc. sizes of the style containing thermometer and capillary side arm are quite serviceable, and the 5, 2, and 1 cc. sizes of the style containing a perforated stopper are useful in examining essential oils, unsulfonated residues, water, etc., when only small quantities of these constituents are available. In some cases a small volumetric flask is made to serve as a pycnometer, as for instance in the distillation and estimation of alcohol from alcoholic liquids.

It is seldom necessary to determine the specific gravity of any solid insecticides or constituents thereof. In all specific gravity determinations, close attention must be given to the temperature. In general, they should be made at the temperature for which the instrument used has been calibrated, frequently 20° C. If for any reason the determination is made at some other temperature, correction must be made. All reports of specific gravity determinations should be accompanied by a statement of the temperature of the material and of the water with which it is compared; 4° C. is the temperature most commonly used for comparison and therefore the specific gravities of liquids are usually designated as sp. gr. t°/4°.

(d) **Refractive Index.**—Refractive indices serve to identify water, oils, and other liquids separated from liquid insecticides during analysis, and they are the principal means of identifying the components of heterogeneous mixtures of solids that are sold as insecticides under proprietary names.

For the determination of the refractive indices of liquids, the Abbé refractometer is entirely satisfactory; it requires only a drop or two of material and has ample range for all liquids likely to be encountered in work with insecticides. The determination of the refractive index of

solid materials, however, is more difficult. The only method suitable for the small particles present in powdered insecticides requires a set of liquids of known refractive index, with which the material is compared under a microscope. The solid particles are considered to have the same refractive index as the liquid in which they are least visible. Since most materials are anisotropic and therefore have more than one index of refraction, it is necessary for accurate work to use a polarizing microscope in order that the characteristic refractive indices may be selected for measurement. It is evident, therefore, that a knowledge and skill in the use of the petrographic microscope, which the ordinary analyst is not expected to possess, is necessary, but in the hands of a competent microscopist the method permits widespread application. Owing to lack of definite crystalline structure, extreme state of subdivision, and absence of known constants of materials, the method will not yield results in all cases, but it can and does furnish much valuable information.

(e) **Microscopic Examination.**—More extensive use can be made of the microscope in identifying insecticides than the mere determination of refractive index just described. The ordinary compound microscope is used to identify plant materials, to make micro-chemical tests which will aid in the qualitative analysis of a material, and to examine bacteria in the testing of disinfectants. A petrographic microscope can furnish additional data on birefringence, optical character, extinction angles, etc., which frequently provide more certain identification of compounds.

Microscopes should be equipped with at least 16 mm. and 4 mm. objectives and with an oil immersion objective of high numerical aperture if bacteriological work is to be carried on. Several eye-pieces, one of which should contain a scale or grating for measuring purposes, should also be available. These instruments are most serviceable in large laboratories where the services of skilled microscopists are available, as is the case in the laboratory of the Food and Drug Administration.

(f) **Polariscopic Examination.**—The principal use of the polariscope in the analysis of insecticides is for the determination of sugar (which is sometimes used as a bait in household insecticides) and for identifying camphor and various essential oils.

(g) **Melting Point.**—The melting point will be found of great service as a means of identifying constituents which have been separated from mixtures. The customary method of determining melting point is to put the material into a small, thin-walled tube (closed at one end) and to immerse it in a suitable heating liquid in contact with the bulb of a ther-

monometer. The tube is slowly heated, and the temperature at which the material softens or melts is noted.

In some cases this method is unsatisfactory owing to the nature of the material. If enough sample is available the congealing point is determined instead. A test tube is partly filled with the material, which is melted. A thermometer is immersed in the material, and the whole is allowed to cool slowly. The liquid will normally supercool somewhat, and when solidification begins the temperature will rise a degree or two. The maximum temperature reached at this stage is considered to be the congealing point. This method may be advantageously used, for example, in the determination of the purity of naphthalene and phenol.

A prerequisite for satisfactory melting-point determinations is a set of standard thermometers, preferably the short-stem type, with a range of about 50° C. each.

(h) Boiling Point and Distillation Range.—The process of fractional distillation is frequently used in insecticide analysis. The boiling points of the fractions obtained also frequently serve to identify particular components, such as carbon disulfide, carbon tetrachloride, etc. Usually distillations are made from side-neck distilling flasks, and ordinary straight condensers are sufficient, but occasionally it is necessary to use one of the more efficient fractionating columns.

Vacuum distillation is seldom required, but steam distillation is frequently used, as in the recovery of nicotine, phenols, etc.

(i) Sublimation.—The uses for sublimation in the analysis of insecticides are not numerous. The principal materials regularly recovered by this process are naphthalene and paradichlorobenzene. Any standard form of sublimation apparatus is suitable; even the use of two watch-glasses ground to fit along the edges may be made to furnish satisfactory results.

(j) Degree of Fineness.—Whereas the toxicity of an insecticide to insects and its harmlessness to plants or animals are primarily dependent upon the chemical nature of the material, its commercial application may be largely influenced by its physical condition. Undoubtedly the most important physical characteristic is the degree of subdivision. Materials designed for use as aqueous suspensions for spraying trees must be powdered finely enough to pass freely through the spray nozzles, must suspend fairly well in water, and must distribute well when applied to foliage. Materials intended for dusting purposes must flow freely through the dusting machines, and must approximate roughly a certain optimum fine-

ness so that they will distribute well without drifting too far before settling.

Numerous attempts have been made to measure the rate of settling of spray materials, but most investigators have worked with too great concentrations and have measured rate of packing rather than rate of settling. However, with the use of power-driven agitators, the question of suspending power has become of minor importance, and no method of determination has attained sufficient importance to become generally used.

With the increase in the use of dusts, however, the particle size or degree of fineness continues to be of considerable interest, and its determination is at times important. Unfortunately, the obvious method of determining it—sifting in a set of standard sieves—is not serviceable. Although Paris green at times will show as much as 50 per cent retained on a 325-mesh sieve (the finest mesh ordinarily obtainable) and hence be subject to a more or less satisfactory screen analysis, calcium arsenate and lead arsenate are ordinarily so finely ground that all but a small per cent will pass the 325-mesh sieve, and hence sifting serves simply to prove that the particles are very small. Even to arrive at this conclusion requires that the material be washed through the sieves with a suitable liquid, since an attempt at dry sifting results in a balling-up of the material and a clogging of the sieve which it is practically impossible to overcome.

Of the many indirect methods that have been proposed and used for particle size determination, perhaps those most suitable for insecticide analysis are the ones based upon elutriation or sedimentation under controlled conditions. Elutriation leads to a separation of the material into fractions in the same manner as sifting, and a knowledge of the rate of sedimentation can be made, by mathematical considerations based on Stoke's law, to yield a complete size-frequency distribution curve, as shown by Odén. For such purposes, liquids that do not affect the product and that cause it to deflocculate as much as possible should be used. Alcohol has been found to be fairly suitable for calcium arsenate and lead arsenate. However, these methods have attained no general use in insecticide analysis.

A more convenient, but much less accurate method, of judging the fineness of a powdered material consists in measuring the apparent volume occupied by a given weight of the material when the latter is introduced into a measuring apparatus in some specific manner. Powdered materials do not completely fill the space they appear to occupy, for two reasons—first, the particles are irregular and do not stack up regularly, and second,

they are surrounded by adsorbed air which tends to further separate them. The proportion of adsorbed air is a function of the surface of the product, and since the latter increases with increasing fineness, the apparent volume occupied by a material is greater the more finely it is powdered. Thus the apparent volume may be used as an approximate measure of the fineness of a material.

It has been used in this way in the insecticide industry. When calcium arsenate became important as a means of controlling the cotton boll weevil, its suitability for dusting was found to be a function of its fineness, and the Delta Laboratory of the Bureau of Entomology adopted the apparent volume as a measure of the latter. One state adopted a law prescribing a certain figure for calcium arsenate, and the idea spread until it was applied to other products intended for dusting. At present apparent volume is not considered so important as formerly, but it still serves a useful purpose.

The method and apparatus used at the Delta Laboratory may be briefly described as follows:

Two ounces of material is put into a cylindrical holder about 2 in. by 9 in., in the axis of which is a $\frac{3}{8}$ in. tube perforated by numerous small holes. The open end of the cylinder is closed by placing over it a disc of filter cloth, weighted with a metal ring, to protect the operator from dust, and air is forced through the central pipe by means of an air pump mounted on the base of the instrument. Twenty vigorous strokes are taken on the pump, and then the cover is removed very carefully to prevent any repacking of the material by jarring, after which the volume occupied by the material is measured by means of an adjustable gage. The gage is graduated to read cubic inches per pound when its cross arm lies across the top of the cylinder and its foot just touches the surface of the powder. An additional ten strokes of the pump are then taken to prove that the maximum volume has been attained. The accepted figure for calcium arsenate is 80-100 cubic inches per pound.

CHAPTER IV

WATER

The water content of insecticides varies from a few tenths of one per cent in powders to as much as 99 per cent in aqueous solutions. That occurring in powders may be present as absorbed or adsorbed moisture; as water of combination in hydrated lime or other hydroxides; as water of crystallization in salt hydrates; or as water of constitution, as in di-lead arsenate.

The water in paste samples is present in such quantity that the material of the sample is actually wetted and assumes a pasty condition. In emulsions the water is present in large quantity; it is ordinarily the continuous phase in which the other immiscible liquid is finely dispersed and the mixture stabilized by an emulsifying agent. In a few instances, as in salves and ointments, the water is the discontinuous phase. In aqueous solutions the water is the predominant constituent, acting as a solvent for soluble salts.

It is the custom to report small quantities of water as percentages of "moisture," while larger quantities are designated as "water." There is no definite dividing line between these two designations, but in general the water contained in powdered material may be considered as "moisture," and that in paste materials, emulsions, aqueous solutions, etc., as "water."

In Powders.—The water in powders is usually determined by a simple procedure. From 1 to 5 grams of the sample is dried to constant weight at atmospheric pressure and at 100°-110° C. The time of heating required to reduce the sample to constant weight is usually 2-5 hours, but in exceptional cases a longer period may be required. The percentage loss in weight is reported as moisture. If the sample contains ingredients that decompose or oxidize when heated in air, the drying must be carried out in a vacuum oven which allows the moisture to be removed at a lower temperature. The water in powdered insecticides is only occasionally determined by drying over a desiccating agent at room temperature.

The combined water in samples of insecticides is usually held more firmly than the absorbed water. Moisture determinations made by drying at 105° C. may include a part of the water of crystallization and hydration, but they rarely include any of the water of constitution.

In samples containing no volatile constituents other than water, the following method, first used by G. J. Brush and extended by S. L. Penfield,¹ gives excellent results and has the advantage of giving the water directly instead of by difference:

The sample is heated in a narrow glass tube (*B* Fig. 1), which has a bulb blown on its closed end and another farther up the tube to hold the condensed water and prevent it from running back and cracking the hot glass. The tubes must be thoroughly dried by heating and aspiration before being used. A piece of capillary glass tubing, (*C*), fitted to the end of the main tube by a rubber connection serves as a stopper to prevent loss of water vapor by convection currents. The tube is held horizontally and the bulb containing the sample is carefully heated with a Bunsen burner. During the heating a piece of asbestos board, (*D*), is placed between the bulb containing the sample and the condensation bulb to prevent loss of water from the latter. The receiving bulb is covered with wet cloth or filter paper and kept wet with cold water as a condensing agent during the heating. When no more water collects in the receiver the tube is softened by heat between the two bulbs, and the bulb containing the residue is pulled off. The tube is then cooled, wiped dry on the outside and weighed, after which it is emptied, dried and again weighed. The difference in weight represents the water in the sample. The identity and purity of the water obtained may be checked by a determination of its refractive index, which should be 1.333 at about 20° C. The thistle tube *A*, Fig. 1, is used to introduce the sample into the lower bulb of the tube *B*.

In Pastes.—The solid components of samples in paste form are likely to settle out, causing unevenness in composition. Care is therefore necessary to secure a uniform sample before proceeding with the analysis. The entire contents of the package should be transferred to a mortar or pan and thoroughly mixed, care being taken to incorporate any liquid that may have separated. A charge of 100 grams is then quickly weighed into a tared crystallizing dish of about 10 cm. diameter and heated on a steam bath until most of the water is expelled. The dish is then removed to an oven, and the heating is continued at 100°-105° C. until the sample is dry enough to powder readily. The loss in weight is noted, the partially dried sample is powdered, and the remaining moisture is determined by drying a weighed portion of about 2 grams of the powder to constant weight at 105° C. The total moisture is obtained by calculation from these two results. In drying samples like paste Bordeaux mixture or other materials containing free lime, which absorb carbon dioxide during drying, correction must also be made for the carbon dioxide taken up by determining it before and after drying.

¹ *Int. J. Sci.*, 3 d series, 46, 31 (1894); *Z. anorg. Chem.*, 7, 22 (1894).

The water in soaps is best determined by distillation with a liquid immiscible with water, such as xylene or toluene, an apparatus, Fig. 2, of the type described by Dean and Stark¹ being used. Several pieces of lump rosin are added to prevent foaming. The volume of the water is meas-

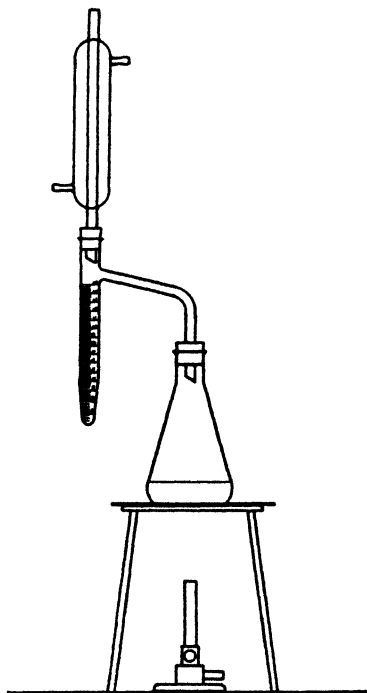


FIG. 2.—Dean and Stark Apparatus for Water Determinations.

ured, and from this volume the percentage of water is calculated on the basis that 1 cc. = 1 gram. The identity and purity of the water obtained may be checked by determining its specific gravity and refractive index.

In Emulsions.—Emulsions are usually handled by the method described for soaps. Foaming is not so pronounced, because smaller quantities of soap are present, and a much smaller quantity of lump rosin will suffice to prevent it. The carbide method may also be used for the determination of water in emulsions.

In Solutions.—The simplest way to determine the water of solutions is to evaporate a portion of the sample in a weighed dish on a steam bath

¹ *J. Ind. Eng. Chem.*, **12**, 486 (1920). *J. Assoc. Official Agr. Chem.*, **9**, 28, (1926).

and then dry the residue to constant weight in an oven. The loss in weight may be regarded as the quantity of water in the sample. The method is only applicable, of course, in the absence of other constituents volatile at the temperature of drying, and it should also be borne in mind that the salts present in some samples will retain water of crystallization when dried at 105° C.

Distillation with a liquid immiscible with water, such as xylene or toluene, can be used for the determination of water in solution, except in the case of solutions containing salts that retain water of crystallization under these conditions. For many solutions containing salts that hold tenaciously to water of crystallization the Penfield method previously described will prove satisfactory if the heating is carried out slowly and carefully.

By "Difference."—In many cases a direct determination of water may be difficult or even impossible. In such cases it may be estimated by difference if the remainder of the analysis is sufficiently complete.

CHAPTER V

ARSENICALS

Many species of insects cause damage to agricultural crops by devouring the foliage. These are referred to as leaf-eating insects. Such insects are ordinarily controlled by the use of stomach poisons, dusted or sprayed upon the foliage and subsequently ingested by the insects during their feeding. Of the materials suitable for use as stomach poisons, the compounds of arsenic have always held first place. Paris green was first used against the potato beetle about 1862, and by 1874 it was being used throughout the country for this purpose. Lead arsenate was adopted in 1894, when the Gypsy moth became a pest in New England, and calcium arsenate has in the last 10 or 15 years become the standard material for use against the cotton boll weevil in the southern part of the United States. In addition to these three prominent arsenical compounds, many others are now being used or have been used in smaller quantities or for special purposes. At the present time the making of arsenical insecticides absorbs a large proportion of the total output of white arsenic.

Because the arsenic of such insecticides is the most important constituent, the arsenical insecticides will be considered as a group, and both general and individual methods for their analysis will be given.

GENERAL METHODS OF ANALYSIS

Preparation of Sample.¹—Thoroughly mix all samples before analysis. Make water-soluble arsenic determinations on samples as received without further pulverization or drying.

Moisture.¹—The official method is applicable to all powdered arsenical insecticides.

Dry 2 grams to constant weight at 105°-110° C. and report the percentage loss as moisture.

Total Arsenic.—*Cuprous Chloride Distillation Method.*¹—This method is applicable to practically all inorganic arsenic compounds and mixtures containing them. *Nitrates interfere* by forming nitrosylchloride, which distills along with the arsenic and slowly oxidizes some of it, giving low results if the arsenic is titrated directly, as directed in the method.

A portion of sample containing about 0.4 gram of arsenic (As) is mixed with an excess of cuprous chloride and heated in a distilling flask with concentrated hydrochloric acid. Any arsenate present is reduced to arsenite by the cuprous salt, and arsenious chloride then distills and is caught in a receiver containing water.

¹ *Methods of Analysis, A. O. A. C.*

The arsenic in the distillate is estimated either iodometrically, after neutralization with sodium bicarbonate, or by direct titration with a bromate solution. Both iodine and bromate solutions may be standardized against chemically pure arsenious oxide, standard samples of which are now procurable from the U. S. Bureau of Standards. The end point in the bromate titration may at first seem somewhat difficult to recognize, but when the proper technic is once acquired this titration is to be preferred to the one in which iodine is used.

This method gives no information concerning the valence of the arsenic in the sample. The titration is calculated to As_2O_3 or As_2O_5 , according to the form known to be present.

*Hydrazine Sulfate Distillation Method.*¹—This method is applicable to most inorganic arsenicals and mixtures containing them. *Nitrates do not interfere*; they are probably reduced to gaseous nitrogen.

This method is to be carried out like the one just described except that a mixture of hydrazine sulfate and sodium bromide is substituted for the cuprous chloride. This mixture is very rapid in its reducing action, and effectually takes care of moderate quantities of nitrates which may be present in some arsenicals.

The foregoing methods for the determination of total arsenic are generally applicable and are capable of the highest accuracy. They should be used in all cases in which the analysis is highly important or likely to be questioned, except in the presence of large quantities of organic matter that may be encountered in many proprietary mixtures such as poisoned bran, tobacco preparations, etc. In such cases aldehyde (furfurol) is probably formed by the action of the concentrated acid on the cellulose materials and being volatile distills along with the arsenic, thereby causing high results when the distillate is titrated with an oxidizing solution. Tobacco powder, especially, seems to produce this effect. Correct results may be obtained by the following modification:

The distillate is made to volume, and an aliquot is evaporated to fuming with sulfuric and nitric acids to destroy the organic materials which have distilled. The arsenic is oxidized by this procedure and must be reduced again before it can be titrated. The reduction and titration are carried out as described under the Gooch-Browning method (p. 494).

The distillation method, using hydrazine, has the advantage in that the residue from the distillation is suitable for further analysis. All the common metals and metalloids other than arsenic are non-volatile under the conditions prescribed in the method, and evaporation of the residue to dryness with nitric acid will destroy both the hydrazine and the bromide and leave the other constituents for further analysis. If hydrobromic acid is substituted for sodium bromide, even the alkalis may be determined. The removal of arsenic from a complicated mixture by this means is far su-

¹ *Methods of Analysis*, A. O. A. C.

perior to its separation as sulfide, especially when the arsenic is present as arsenate.

Two other methods of less general applicability deserve mention.

Gooch-Browning Method.—This method is fully described in the official method for water-soluble arsenic.¹ The sample is dissolved in dilute sulfuric acid, the arsenic is reduced by boiling with potassium iodide, and the reduced solution is titrated with standard iodine after it has been made alkaline with sodium bicarbonate. This method is directly applicable to white arsenic, arsenic acid, calcium arsenate, magnesium arsenate, and zinc arsenite. It is not applicable to Paris green because of the reducing action of iodides on cupric copper, and to lead arsenate because of the formation of yellow lead iodide. The method is adaptable to lead arsenate if the latter is dissolved in nitric acid and fumed with sulfuric acid and the lead sulfate is filtered off.

Further, the method gives high results in the presence of other polyvalent metals such as iron and antimony, but in well-made standard arsenical insecticides the percentage of these impurities present is small, and the method is useful when speed and convenience are more desirable than extreme accuracy. Small proportions of nitrates do not interfere as they are destroyed during the boiling with potassium iodide.

*Thiosulfate Titration Method.*¹—This method is of still more limited applicability, being suitable only for arsenates.

The sample is dissolved in concentrated hydrochloric acid and evaporated to dryness to destroy any nitrates that may be present. The residue is redissolved in concentrated hydrochloric acid, potassium iodide is added to reduce the arsenate, and the liberated iodine is titrated, after moderate dilution, with standard sodium thiosulfate solution.

This method is applicable to calcium and magnesium arsenates, and to lead arsenate if ammonium chloride solution is added to keep lead iodide from precipitating. Like the previous method it gives high results in the presence of ferric iron and pentavalent antimony. The method will be found especially useful when large numbers of analyses of high-grade materials are to be made.

Water-Soluble Arsenic.—It is well recognized that while many insoluble compounds of arsenic may be safely applied to foliage, the soluble compounds of this element produce severe injury. Hence a knowledge of the proportion of water-soluble arsenic is of great importance and this constituent should always be determined.

The estimation of water-soluble arsenic in an insecticide could be carried out with any weight of sample and in any one of a number of ways if the insecticide itself were wholly insoluble and the soluble arsenic were due entirely to a freely soluble compound of arsenic present as an impurity. This is approximately the case with lead arsenate. However, if the arsenical compound itself possesses an appreciable solubility, if it is hydrolytically decomposed by water as is Paris green or if it has to be used in admixture with excess base as is the case with calcium arsenate and magnesium arsenate, it is plainly evident that at least the proportion

¹ *Methods of Analysis*, A. O. A. C.

of sample to water must be specified in order that a statement of the percentage of water-soluble arsenic may have any meaning. Further, since both solubility and degree of hydrolysis vary with temperature, it is also necessary to adopt a fixed temperature at which the extraction is to be made. Thus the determination of water-soluble arsenic becomes an entirely empirical matter.

The first method proposed for the estimation of this constituent in lead arsenate and Paris green (at that time the most important arsenical insecticides) called for the extraction of 2 grams of sample with 2 liters of water for a period of 10 days.¹ This procedure proved too time-consuming, and as the empirical nature of the method was recognized the period of digestion was reduced. The method as now used may be briefly described as follows: Two grams of powdered material (or 4 grams if in paste form) is extracted with 1 liter of recently boiled and cooled distilled water for a period of 24 hours at a temperature of 32° C. with vigorous shaking at 1 hour intervals during the working day. The filtrate from this extraction is analyzed for arsenic by the Gooch-Browning method, which has been outlined under Total Arsenic.

This method naturally gives only the value of the total arsenic in water-soluble form. If the product being tested is a mixture of arsenate and arsenite and it is desired to determine the proportions of each that are soluble, a second aliquot of the extract can be treated with sodium bicarbonate and titrated directly with standard iodine solution. This gives the soluble arsenious oxide, and the difference between this and the total will be the soluble arsenic oxide.

As stated previously, the method of extraction is empirical, and the directions must be closely followed to get reproducible results. However, a fluctuation of $\pm 1^\circ$ C. in the temperature is of no consequence, and this degree of accuracy is easily attained by the use of a gas burner controlled by a toluene-filled regulator, in an open tank without a stirrer. It is immaterial at what time the extraction is started—that is, whether the shaking is done at the beginning, middle, or end of the total period of 24 hours.

Practically all the investigators that have sought to simplify the extraction of water-soluble arsenic have directed their attention to lead arsenate, which because of its extremely low solubility and slight hydrolysis² is most likely to furnish the same results by different methods. Curry and Smith³ suggested 18 hours' continuous shaking at 20° C. and a correction for the solubility of the lead arsenate itself; Tartar and Robinson⁴ poured hot water through a filter containing the sample; Gray and Christie⁵ and Scholz and Waldstein⁶ recommended boiling the sample for a short time

¹ U. S. Dept. Agr. Bur. Chem. Bull. 107, revised, 240.

² McDonnell and Graham, *J. Am. Chem. Soc.*, **39**, 1912-18 (1917).

³ *Ind. Eng. Chem.*, **4**, 198 (1912).

⁴ Oregon Agr. Coll. Expt. Sta. Bull. **128** (1915).

⁵ *Ind. Eng. Chem.*, **8**, 1109 (1916).

⁶ *Ibid.*, **9**, 682 (1917).

with water; and Roark¹ showed that a short boiling method is applicable to zinc arsenite as well as to lead arsenate.

At times, during the determination of the dissolved arsenic by the Gooch-Browning method, when the attempt is made to dispel the slight quantity of iodine left after the reduction with potassium iodide, it is found impossible to make the solution water-white. The persistent yellow color, which is probably due to undissociated antimony iodide, can be remedied by further dilution, which permits the antimony iodide to ionize into colorless ions. In such cases the results will be high, since antimony titrates in this method exactly as does arsenic.

The methods most commonly used for the analysis of the individual arsenical compounds follow, and discussions of mixtures appear later in other sections.

WHITE ARSENIC (ARSENIOUS OXIDE)

White arsenic, or arsenious oxide (As_2O_3), is a by-product of the smelting of ores of copper, lead and zinc. The arsenic occurring in the ores as arsenides of the various metals, principally mispickel (FeAsS), is oxidized during the smelting operation and the arsenious oxide being volatile is carried away with the flue-gases. The latter are led through large chambers, where certain constituents, including the arsenious oxide, condense as flue-dust. This deposit is resublimed once, and the sublimate, containing 98 per cent arsenious oxide, forms the white arsenic of commerce.

Although arsenious oxide exists in several allotropic forms, the ordinary commercial material, at least in the United States, is always the octahedral variety. The product is often a heavy coarsely crystalline powder, and at other times a rather light powder with much less marked crystalline appearance, these differences being due, no doubt, to the conditions of condensation after sublimation.

White arsenic itself is not used as an insecticide on plants to any great extent because it is soluble enough in water to kill or cause serious damage to most kinds of foliage. It is used in baits for poisoning grasshoppers and cutworms, and in fly poisons. Its main importance from an insecticidal viewpoint is due to its use as the source of arsenic for practically all other arsenical insecticides.

¹ *J. Assoc. Official Agr. Chem.* **7**, 322 (1924).

The complete analysis of white arsenic for all its minor constituents is a long, involved process, and need not be considered in a work of this kind. Only the principal determinations will be described.

Moisture.—White arsenic is not hygroscopic and seldom contains more than 0.2 per cent moisture, so that normally it is not necessary to make a determination of this constituent. However, when desirable it may be determined by drying to constant weight in an air oven at 105°–110° C., and by weighing at intervals of 2 or 3 hours until the weight is constant.

Total Arsenic.—If the qualitative tests show the presence of appreciable quantities of impurities the simplest method of determining the arsenic content is either by the cuprous chloride or hydrazine sulfate distillation method previously described. In view of the high purity of this product, the portion analyzed should be such as to give nearly 50 cc. titration in order to minimize the error. The result should be calculated to arsenic trioxide unless the qualitative test shows an appreciable quantity of arsenic pentoxide.

In the absence of any marked quantity of impurities, the arsenic content may be estimated by the following simple method.

Dissolve 2 grams of the sample by warming with 25 cc. of 10 per cent sodium hydroxide solution, transfer to a 250 cc. volumetric flask, acidify with sulfuric acid, and dilute to the mark. After thoroughly mixing, remove a 25 cc. aliquot, neutralize with sodium bicarbonate, add an excess of this reagent, and titrate with standard iodine solution; or take a 25 cc. aliquot, add 15 cc. of concentrated hydrochloric acid, dilute to 100 cc., warm to 90° C., and titrate with standard bromate solution as described in *Methods of Analysis, A. O. A. C.* Calculate the result to percentage of arsenious oxide (As_2O_3).

It is important that the value of the standard iodine solution used in the titration of materials of such high arsenic content as this be determined with great accuracy, and it is recommended that the standard sample for comparison be very carefully prepared and tested, or that the material now offered by the Bureau of Standards be used.

This second method gives only the arsenious oxide content of the material. If the qualitative test has shown appreciable arsenic oxide, and it is desired to estimate both forms, another 25 cc. portion may be reduced with potassium iodide as in the Gooch-Browning method, and the total arsenic determined by titration with standard iodine solution. This total arsenic less that present as arsenious oxide will give the quantity present as arsenic pentoxide (As_2O_5).

Qualitative Tests for Impurities.—It is frequently desirable to supplement the arsenious oxide determination by qualitative tests for some of the more commonly occurring impurities. A portion of the sample is dissolved by warming with caustic soda solution and used to test for the following impurities:

Sulfides.—The alkaline solution when tested with caustic soda solution of lead acetate will show a black precipitate if sulfur or a sulfide is present.

Antimony.—The addition of a large volume of water will produce a cloudiness if antimony is present.

Heavy Metals.—Hydrogen sulfide will produce a black precipitate if bismuth, copper or lead is present.

Arsenic Oxide.—This may be tested for by extracting a portion of the sample with 50 per cent ethyl alcohol and testing with a silver nitrate solution. A characteristic reddish brown precipitate indicates the presence of pentavalent arsenic.

Mercury.—This may be present in white arsenic. It has a special significance in that its presence in very minute quantity very markedly reduces the speed of reaction when the white arsenic is subjected to oxidation with nitric acid in the manufacture of arsenic acid. A suitable method for the detection of this impurity has been published.¹

Water-Soluble Arsenic.—The determination of water-soluble arsenic in a sample of white arsenic is practically meaningless. The solubility of arsenious oxide in water amounts to about 25 grams per liter at 32° C., and it would appear at first sight that the use of 1 or 2 grams per liter, as prescribed in the A. O. A. C. method for water-soluble arsenic, would result in complete solution of the sample and hence a result of 100 per cent. Such is not the case, however. The establishment of equilibrium from the unsaturated side is very sluggish and erratic, and results running from 20 to 60 per cent may be obtained on different samples. Furthermore, duplicate determinations seldom agree well and consequently the determination is valueless. From the insecticidal viewpoint it is proper to consider arsenious oxide entirely soluble in water.

ARSENIC ACID

Arsenic acid itself is used as an insecticide even less frequently than white arsenic, but owing to its importance in the manufacture of the metallic arsenates it is necessary that brief consideration be given to it.

It is made by the oxidation of white arsenic. The oxidizing agent generally used is nitric acid, and the operation is carried out in a stoneware or duriron vessel connected to an absorption system for the recovery of the nitric acid. This is somewhat similar to the recovery system used in the manufacture of sulfuric acid by the chamber process. By heating and perhaps blowing to remove the last of the nitric acid, the arsenic acid is obtained in the form of a sirupy solution containing about 60 per cent arsenic oxide (As_2O_5). It is possible to prepare solid arsenic acids of the composition $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ and $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, and some material in this form has been imported.

The only determination usually necessary for this product is that of the arsenic acid content. It may be estimated by the Gooch-Browning method or by one of the distillation methods. It may at times be desirable to test qualitatively for the presence of unoxidized arsenious acid and for nitric acid.

Qualitative Test for Nitric Acid.—Acidify a portion of the arsenic acid with hydrochloric acid, add a drop or two of methyl orange, and heat the mixture. If

¹ *J. Ind. Eng. Chem.*, **16**, 1168 (1924).

nitric acid or its oxides are present in more than mere traces, the methyl orange will be destroyed. Or mix a small portion of the acid in a test tube with two or three times its volume of concentrated sulfuric acid and add a few drops of phenol-disulfonic acid. Pour the mixture into water and make alkaline with ammonia. A yellow color indicates nitric acid, and the intensity of color is in proportion to the quantity of nitric acid present.

Qualitative Test for As_2O_3 .—Make a sample of the acid alkaline with sodium bicarbonate and test with iodine solution. Absorption of iodine indicates arsenious oxide. A quantitative determination may be made by using weighed samples and standard iodine solution.

PARIS GREEN

Paris green was the first arsenical insecticide to come into extensive use. It was introduced about 1862 as a means of combating the ravages of the Colorado potato beetle and has held its place in potato culture since that time. About 8 million pounds were used in the year 1927.

Chemically, Paris green is cupric aceto-arsenite and is represented by the formula $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$. Theoretically it should contain 58.55 per cent arsenious oxide (As_2O_3), 31.39 per cent cupric oxide (CuO) and 10.06 per cent acetic anhydride $[(\text{CH}_3\text{CO})_2\text{O}]$. The products encountered on the market approximate this composition, but practically all samples contain small quantities of sodium sulfate, the result of incomplete washing of the material during manufacture.

Paris green is generally made by dissolving white arsenic in sodium carbonate solution, adding the proper quantity of copper sulfate, which results in the precipitation of an arsenite of copper, and then making the whole acid with acetic acid. The Paris green formed is a heavy dark green material, which is washed by decantation or simple filtration.

The principal determinations to be made on Paris green are total arsenic, arsenic present as arsenious oxide, water-soluble arsenic, and sodium sulfate when a qualitative test shows it to be present in appreciable quantity. Copper is determined less frequently, and the acetic acid practically never.

Total Arsenic.—This constituent is most simply estimated by the hydrazine distillation method described under General Methods and in *Methods of Analysis*, A. O. A. C.

Total Arsenious Oxide.¹—This constituent is determined by dissolving the sample in sulfuric acid and titrating an aliquot either directly with standard bromate solution or with standard iodine after neutralization with sodium bicarbonate. The insecticide act requires a minimum of 50 per cent As_2O_3 .

¹ *Methods of Analysis*, A. O. A. C.

Water-Soluble Arsenic.—The quantity of arsenic in water-soluble forms found in Paris green exceeds that encountered in most other standard agricultural insecticides. This is due to the fact that water hydrolyzes the material, the degree of hydrolysis being dependent on the temperature and the time of extraction. The legal requirement is that the water-soluble arsenious oxide shall not exceed 3.5 per cent, and properly manufactured material will not exceed this quantity.

Uncombined Arsenious Oxide.—In the early days of the manufacture of Paris green the product at times contained uncombined arsenious oxide, recognizable by aid of the microscope. To distinguish this constituent from the soluble arsenic due to hydrolysis a method was used in which a sample was extracted with a concentrated sodium acetate solution. The high concentration of the acetate ion repressed the hydrolysis, and only the free white arsenic dissolved. However, Paris green as made at present rarely contains an appreciable quantity of uncombined white arsenic, and the method has been practically abandoned.

Sodium Sulfate.—If an aqueous extract of a sample of Paris green, when acidified and tested with barium chloride solution, shows an appreciable quantity of sulfate ion, it may be desirable to determine the quantity present. The following method may be used:

Put 4 grams of material into a 200 cc. volumetric flask; add 0.1 gram of calcium oxide, and fill the flask to the mark with water. After allowing to stand with frequent shaking for about 30 minutes, filter the liquid through a dry filter and use the filtrate for the determination of both sodium and sulfate. Determine the sulfate in a 50 cc. aliquot by precipitation as barium sulfate, and estimate the sodium in a 100 cc. aliquot after the removal of arsenic with hydrogen sulfide and the removal of other metals with ammonia and ammonium oxalate.

Total Cupric Oxide.—This determination is seldom required. It may be made by one of the methods given in *Methods of Analysis*, A. O. A. C., in which the sample is boiled with sodium hydroxide solution to precipitate the copper as cuprous oxide, which is then filtered and dissolved in nitric acid, and the copper estimated either electrolytically or by the thiosulfate titration method.

Acetic Anhydride.—The proportion of acetic anhydride in Paris green is seldom determined. However, it may be estimated by distilling a phosphoric acid solution of the sample with xylene and titrating the acetic acid in the distillate, as proposed by Pickett.¹

LEAD ARSENATE

When it became necessary to combat leaf-eating insects attacking plants having more tender foliage than that of the potato plant, investigators sought to find arsenicals that were less soluble than Paris green. Following the appearance of the Gypsy moth in New England, Moulton experimented with various materials and then chose lead arsenate as the most suitable. Since that time the use of this compound has continually increased, and it is today the most important agricultural arsenical. At present, about 27 million pounds of it are used annually in the United States.

¹ *J. Ind. Eng. Chem.*, **12**, 570 (1920).

At first lead arsenate was made by double decomposition between soluble lead salts and sodium arsenate. Other simpler methods were developed later, and at present the bulk of it is made by the direct union of litharge and arsenic acid under the influence of a "catalyst," such as a small proportion of acetic or nitric acid. In this method the catalyst is the only by-product of the reaction, and the washing of the compound is a simple matter. For a long time the lead arsenate was pressed but not dried, and was sent into commerce in the form of a paste containing 50 per cent water. Now, however, 98-99 per cent of it is dried and ground and appears on the market as a fluffy white powder.

The Federal Insecticide Act describes lead arsenate as the product formed by the replacement of one, two or three of the hydrogen atoms of ortho arsenic acid (H_3AsO_4) by lead, indicating that there are three forms of lead arsenate. However, monolead arsenate ($\text{PbH}_4(\text{AsO}_4)_2$) was made (subsequent to the passage of the act) and found to be very unstable, because in water it decomposes completely into dilead arsenate (PbHAsO_4) and arsenic acid. For this reason it cannot be used for insecticidal purposes.

The lead arsenate that is produced by the most common commercial method described above is essentially dilead orthoarsenate (PbHAsO_4), and high grade commercial materials correspond closely to this composition. It forms by far the larger portion of the lead arsenate used commercially and is the compound usually meant when the term "lead arsenate" is used without qualification. Another form of lead arsenate used to a limited extent is made by the action of ammonia on dilead arsenate; for a long time it was thought to be trilead orthoarsenate ($\text{Pb}_3(\text{AsO}_4)_2$), the third member of the group of orthoarsenates. It is now known that trilead arsenate is very unstable and that the commercial product long thought to be this compound is a basic lead arsenate of the composition represented by the formula $\text{Pb}_4(\text{PbOH})(\text{AsO}_4)_3 \cdot \text{H}_2\text{O}$.¹ The use of this material is limited to the Pacific coast, where climatic conditions are such that dilead arsenate sometimes causes burning of foliage.

Both forms of lead arsenate are amenable to the same methods of analysis, and therefore they will be treated together.

Moisture.²—As previously noted, lead arsenate was first used in the form of a paste adjusted to contain approximately 50 per cent of water, but such a product is only occasionally encountered today. In such cases the entire sample must be

¹ *J. Am. Chem. Soc.*, **38**, 2016, 2034 (1916); **39**, 940 (1917).

² *Methods of Analysis*, A. O. A. C.

particularly well mixed to overcome the natural tendency to separate, and a large sample (50–100 grams) is taken for the water determination, not only to decrease the error of sampling but to give sufficient dry material with which to carry out the remainder of the analysis. The large samples are dried on the steam bath and carefully broken up with a spatula, and the drying is completed in an air oven at 105°–110° C. The dried material is bottled for use. If the sample is a powder, a small sample of 1 or 2 grams is used for a moisture determination by the usual process.

Total Arsenic.¹—Apply any one of the methods described under “General Methods.”

Arsenious Oxide.—Lead arsenate may be contaminated with lead arsenite, when arsenic acid containing unoxidized white arsenic is used.

Qualitative Detection—Boil a portion of the sample with dilute acetic acid containing a small quantity of lead acetate. Filter and add bromine water to the clear filtrate. A white precipitate is evidence of arsenite. (This test depends on the fact that lead arsenite is soluble and lead arsenate insoluble in acetic acid. The bromine serves to oxidize the former to the latter.)

Quantitative Determination—Boil the sample with dilute sulfuric acid in a volumetric flask, cool, make to mark, and filter. Neutralize an aliquot of the filtrate with sodium bicarbonate and titrate with standard iodine solution.

Water-Soluble Arsenic.—Pure dilead arsenate is only very slightly soluble in water and the basic form even less so. It is only because of the chance that other soluble arsenic compounds are present as impurities that a water-soluble arsenic determination is necessary with this material. The determination is made as outlined under “General Methods.”

The Federal Insecticide Act requires that there be less than 0.75 per cent arsenic oxide (As_2O_3) in soluble form. Commercial lead arsenate, as now manufactured, rarely contains this much and frequently the titration is indistinguishable from that of a blank determination. In the latter case it is customary to report a trace, since dilead arsenate is broken up to a slight extent by water.²

Lead Oxide.—Lead may be precipitated and weighed either as lead chromate or as lead sulfate, as described in *Methods of Analysis, A. O. A. C.* Fairly accurate results may be obtained by a modification of the sulfate method in which alcohol is not used.

CALCIUM ARSENATE

The extensive use of Paris green and lead arsenate naturally led to the use of other arsenical compounds. Since lime is the cheapest base available, it was soon suggested as a substitute for the more expensive cupric oxide and litharge, and this led to experiments with calcium arsenate. The discovery that calcium arsenate was effective in the control of the cotton boll weevil stimulated its production, and about 27 million pounds was used in 1927 in the United States.

¹ *Methods of Analysis, A. O. A. C.*

² *J. Am. Chem. Soc.*, **39**, 1912 (1917).

Calcium arsenate is made by a process quite similar to that used in the manufacture of lead arsenate. Quick lime is slaked to a thick slurry with water, and a solution of arsenic acid is added. No catalyzer is needed as in the case of lead, because the oxide of calcium is somewhat soluble, and the reaction proceeds sufficiently fast without it. Careful control of temperature and concentration is necessary for the production of a product uniform in composition and physical properties.

Chemically, calcium arsenate is not a pure product, as is acid lead arsenate. All three ortho arsenates of calcium have been prepared, but none is suitable for use directly as an insecticide. Monocalcium arsenate ($\text{CaH}_4(\text{AsO}_4)_2$) is very soluble in water, the dicalcium arsenate (CaHAsO_4) (corresponding to the lead compound) is extensively hydrolyzed in water, and even the tricalcium arsenate is too soluble for general use, since it shows about 3 per cent water-soluble arsenic oxide by the official method. However, if lime is used in excess of the proportion needed for tricalcium arsenate, the excess lime exercises a strong repression on the solubility, and the resulting mixture is the calcium arsenate of commerce.

In its manufacture the common practice is to use four equivalents of calcium oxide (CaO) to one of arsenic pentoxide (As_2O_5). Some of the excess lime goes to make a basic calcium arsenate, and the remainder appears as free calcium hydroxide. Consequently the finished commercial product is a mixture of one or more calcium arsenates with free calcium hydroxide, calcium carbonate from absorption of carbon dioxide and small quantities of impurities from the lime used.

As ordinarily made, calcium arsenate contains approximately 42 per cent total calcium oxide and 40 to 42 per cent arsenic oxide, the latter being equivalent to 69 to 72 per cent tricalcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$). (It is customary to figure the As_2O_5 to tricalcium arsenate. At the present time the basic arsenates, if they exist at all, are not well understood). By reducing the proportion of lime used, products containing low water-soluble arsenic and as high as 46 per cent As_2O_5 may be made, but approximately 42 per cent is recognized as the safe limit. Other methods of making calcium arsenate have been proposed, and some have actually been used, but they are relatively unimportant at present and need not be described. As in the case of other arsenicals, the principal determinations to be made on calcium arsenate are the total and the water-soluble arsenic. These determinations offer no new difficulties and are the same as used for lead arsenate.

Total Arsenic.—Determine by one of the procedures described under "General Methods," and calculate to arsenic oxide (As_2O_3).

Water-Soluble Arsenic.—Determine as described under "General Methods."

Arsenious Oxide.—Calcium arsenate normally contains very little, if any, arsenious oxide, but the determination of this constituent is necessary at times because products have been encountered which were nothing but mixtures of lime and white arsenic. The method given for this constituent under "Lead Arsenate" is not entirely satisfactory for calcium arsenate, because the large quantity of calcium carbonate formed when the sodium bicarbonate is added makes the attainment of the end point rather sluggish. Titration in acid solution with standard bromate solution is to be preferred. (See *Methods of Analysis, A. O. A. C.*)

Calcium Oxide.—The calcium oxide content of calcium arsenate may be determined without first separating the arsenic if the calcium is precipitated with ammonium oxalate from acid solution. The small quantities of iron and alumina normally present do not interfere, because they do not form oxalate under the conditions of the precipitation.

While the analysis of most calcium arsenates will be confined to the determinations just described, the complicated nature of the material and its increasing importance demand that, at times, a complete analysis be made. In such circumstances, the following additional determinations are required.

Moisture.—Dry 2 grams in an electric oven at 110°C . to constant weight.

Carbon Dioxide.—Use a 2 gram sample and determine by the evolution and absorption method as described in *Methods of Analysis, A. O. A. C.*

Water of Combination.—Ignite a 0.5 gram sample over a blast lamp to constant weight, and from the total loss subtract the loss due to carbon dioxide.

Other Constituents.—When the determination of metals other than calcium is required it becomes advisable to prepare a stock solution from which the arsenic has been removed. Two simple procedures may be followed:

First, a portion of the sample may be treated as in the hydrazine distillation method for total arsenic, except that hydrobromic acid is substituted for the sodium bromide and the reaction is carried out in a beaker under a hood with good draft. The use of hydrobromic acid makes possible the determination of the alkali metals. Evaporation of the residue to dryness with nitric acid destroys both the bromides and the hydrazine salts, leaving the solution ready for the following general method of separation. *Second*, a portion of the sample may be evaporated to dryness on the steam bath several times with a mixture of hydrochloric and hydrobromic acids. These evaporations proceed rather slowly, but when completed there is no hydrazine sulfate to be removed, and further the residue is in condition for the estimation of sulfate if desired.

Whichever procedure is followed, the residue is baked in the oven at 110°C . to render the silica insoluble and then taken up in dilute hydrochloric acid; the silica is filtered off, dried, ignited, and weighed. The filtrate is made to volume in a volumetric flask, and aliquots are used for the determination of the metals by any standard procedure.

An approximate idea of the actual composition of commercial calcium arsenate may be obtained by determining the free calcium hydroxide content according to a

method that has been published.¹ This method is not particularly easy to run or absolutely satisfactory as to results, but it is the only one available.

Physical Character.—In applying calcium arsenate as a dust to cotton plants, it was found that when it was too coarsely powdered it did not distribute well over the plants and that when it was too finely powdered it drifted too far before settling and much of the material was wasted. A method of roughly estimating the fineness, based upon a determination of the number of cubic inches occupied by one pound of material, was developed and is described under Chapter III. A value of 80-100 cubic inches per pound was tentatively adopted as indicating a satisfactory degree of fineness for cotton dusting.

MAGNESIUM ARSENATE

Because magnesium salts are common, it is natural that the demand for new insecticides should lead to the manufacture and use of magnesium arsenate. However, it has found only limited application, being used mainly in the control of the Mexican bean beetle, and its manufacture has not reached very large proportions.

This material is made in the same general way as calcium arsenate—by direct union of magnesium oxide with arsenic acid. Here again it is necessary to have an excess of base over the proportion corresponding to trimagnesium arsenate ($\text{Mg}_3(\text{AsO}_4)_2$), owing to too great solubility of the latter for use on plants. Commercial materials actually run about 6 mols of magnesium oxide (MgO) to one mol of arsenic pentoxide (As_2O_5).

Normally it is considered sufficient in the analysis of this material to determine total arsenic and water-soluble arsenic and in addition the arsenious oxide, if any is suspected or known to be present. These are determined as described under "Calcium Arsenate."

If for any reason the content of magnesium oxide, or a complete analysis, is desired, proceed exactly as under "Calcium Arsenate—Other Constituents," until the arsenic-free stock solution is obtained. Since in this case there will be only small quantities of calcium in the presence of large quantities of magnesium it is necessary to use special precautions in the separation of these two metals. The modified Stolberg method² will be found entirely satisfactory. In this method the sulfates of magnesium and calcium are separated by the action of a mixture of ethyl and methyl alcohols, in which the former is soluble. The calcium is then determined as oxalate and the magnesium as pyrophosphate.

¹ *Ind. Eng. Chem.*, **16**, 950 (1924).

² *J. Assoc. Official Agr. Chem.*, **5**, 401 (1922); *Z. angew. Chem.*, **17**, 769 (1903).

ZINC ARSENITE

Zinc arsenite has been used as an insecticide for the same general purposes for which Paris green is used, but since it has remained relatively unimportant, its analysis will be treated only briefly.

It is prepared commercially by the interaction of zinc oxide with arsenious oxide in the presence of water, followed by filtering, drying and grinding. It has a composition which is approximately that represented by the formula $Zn_3(AsO_3)_2$; it usually contains about 40 per cent of As_2O_3 instead of the 45 per cent corresponding to that formula. It is a white powder, rather heavy and practically insoluble in water. Total arsenic and water-soluble arsenic are the usual determinations made. The determination of zinc is not often required.

Moisture.—Determine in the usual way by drying to constant weight at 105° C.

Total Arsenic.—The simplest method for estimating the total arsenic content is the distillation method, described on pp. 492-3 and in detail in *Methods of Analysis*, A. O. A. C. Calculate the result of the titration to arsenious oxide (As_2O_3), and to zinc arsenite ($Zn_3(AsO_3)_2$). The product will normally show about 40 per cent arsenious oxide, equivalent to 89 per cent zinc arsenite. The remainder consists mainly of zinc oxide, zinc carbonate, and moisture.

Arsenious Oxide.—Ordinarily, the total arsenic in zinc arsenite may be assumed to be in the trivalent form. To verify this determine arsenious oxide by solution of the sample in hydrochloric acid, followed either by direct titration with a standard sodium bromate solution or by the addition of excess sodium bicarbonate and subsequent titration with standard iodine solution.

Conversely, this determination can be ordinarily regarded as giving the total arsenic and may be used for that purpose, but its limitations should be kept in mind.

Arsenic Oxide.—If any appreciable quantity of arsenic in the form of the arsenate is present in zinc arsenite, which is infrequent, it may be estimated as the difference between the total arsenic and arsenious arsenic determined as described above. It may be verified qualitatively by treating a small portion of the sample with insufficient dilute nitric acid for complete solution and adding silver nitrate solution, which will produce the characteristic dark, reddish-brown, silver arsenate.

Water-Soluble Arsenic.—Treat a 2 gram sample with water for 24 hours, as described under "General Methods," and determine the arsenic in the solution, after filtration by direct titration with standard iodine, on the assumption that it is all present in the trivalent form. The quantity is ordinarily very small, and is figured to As_2O_3 .

Zinc Oxide.—The zinc contained in zinc arsenite is determined only as a check on the purity of the product since it is not considered to have any insecticidal action. When desired, it may be estimated by the method described in *Methods of Analysis*, A. O. A. C. In this method the sample is dissolved in hydrochloric acid, and the zinc is precipitated and weighed in the form of a double thiocyanate of mercury and zinc. The method is easily carried out and gives excellent results.

MOLASSES-CALCIUM ARSENATE MIXTURES

Mixtures of calcium arsenate with black strap molasses have been used at times as poisons for control of the cotton boll weevil in the southern states. The proportions used usually approximate 1 part of calcium arsenate to 10 parts of molasses.

The following methods will serve for the analysis of most preparations of this character.

Sampling.—Remove the cover of the container; thoroughly mix the contents, taking care to dislodge any of the calcium arsenate that may have caked on the bottom and to distribute it uniformly throughout the liquid; and rapidly transfer a portion to a smaller container for use in analysis.

Water.—Mix the sample thoroughly and pour off rapidly into a weighed porcelain dish between 50 and 100 grams. Reweigh to determine the weight of sample. Heat the mixture on the steam bath until it appears dry, then transfer to an oven at 110° C., and continue drying at least overnight, or to constant weight. Calculate the total loss in weight to percentage of water.

Total Arsenic.—Mix the sample thoroughly, and pour off rapidly about 50 grams into a weighed beaker and reweigh to determine the weight of sample. Let stand until most of the insoluble matter has separated, then pour the supernatant liquid into a 2 liter volumetric flask and dilute it to about 1 liter. Add 80 cc. of water and 20 cc. of concentrated nitric acid to the residue in the beaker and stir until the residue dissolves. Transfer the liquid to the flask and treat any remaining residue in the beaker with 20 cc. more of nitric acid. Transfer this mixture to the flask, make to volume, and mix well.

Take a 50 cc. aliquot of the solution prepared as described, put it into a 500 cc. Erlenmeyer flask, and add 20 cc. of strong nitric acid and 8 cc. of concentrated sulfuric acid. Evaporate until fuming begins, adding a few drops of fuming nitric acid from time to time to clear up the solution if it goes black. When no further blackening occurs, dilute to about twice the volume and again evaporate to fuming to expel all nitric acid. Dilute the residue to about 200 cc. with water, add 10 cc. of 20 per cent potassium iodide solution, and boil down to about 50 cc. to reduce the arsenic. Cool to room temperature, exactly dispel any remaining iodine by the dropwise addition of 0.5 *N* thiosulfate solution, judging the end point by the color of the solution (do not use starch), dilute to about 150 cc. with water, neutralize with sodium bicarbonate, add about 5 grams in excess, and titrate with 0.05 *N* standard iodine solution, using starch if desired. Calculate the results to percentage of arsenic (As) and to percentage of arsenic oxide (As_2O_3), if it is known that the arsenical used was calcium arsenate. The results are also sometimes figured to tricalcium arsenate, $(\text{Ca}_3(\text{AsO}_4)_2)$, which figure, however, will be only about 70 per cent of the commercial calcium arsenate actually used, since the latter contains excess lime and other impurities. If it is desired to estimate the actual solid matter present, proceed as follows:

Total Insoluble Matter.—Mix the sample thoroughly and pour about 40 grams into a weighed centrifuge tube, obtaining the exact weight by reweighing. Centri-

fuge at high speed for 2 hours, decant the supernatant liquid, and save it for future examination if desired. Wash the deposit by adding water, stirring back into suspension, and again centrifuging. Repeat until one washing is colorless, showing complete removal of the molasses. Discard the washings and dry the tubes and residues to constant weight at 110° C. Calculate the percentage of insoluble matter. This value will be slightly lower than the true percentage of commercial calcium arsenate, since a portion of the lime present will have been dissolved. However, the error will be small.

Water-Soluble Arsenic.—To ascertain how much arsenic is actually present in solution, examine the sirup obtained from the first centrifuging described under "Total Insoluble Matter." Since it is probably more important to employ the same method that is used for other arsenical pastes the following procedure is recommended:

Mix the sample thoroughly, take a portion approximately 4 grams, weigh it accurately, and transfer it to a 1 liter Florence flask with 1 liter of recently boiled and cooled distilled water. Allow to stand 24 hours at 32° C., shaking every hour during the working day. Filter off 250 cc. and treat exactly as described under "Total Arsenic." Calculate to percentage of soluble arsenic oxide (As_2O_3) and to metallic arsenic (As).

CHAPTER VI

COPPER COMPOUNDS

The compounds of copper are important owing to their effectiveness in controlling fungicidal diseases of plants, and it is generally conceded that the copper is the active agent. On the other hand the insecticidal value of copper is low, and Paris green, which was the first arsenical insecticide to be used in large quantities, owes its effectiveness principally if not entirely to its arsenic content.

The fungicidal action of copper was discovered by accident about 1882. Some grape growers in France applied a mixture of copper sulfate and lime to the vines to deter thieves from stealing the grapes. Later it was noticed that the treated vines were much freer from the disease known as downy mildew than the untreated vines. Since that time the use of a mixture prepared by the action of lime on copper sulfate, under the name Bordeaux mixture, has steadily increased, and this material is today the principal agent in the control of many fungicidal diseases. In recent years great progress has been made in the disinfection of seed to prevent the transmission of plant diseases, and for this purpose copper carbonate has been found particularly effective.

Ammoniacal copper carbonate solution, copper sulfate-lime mixture, and combined sprays containing Bordeaux mixture and various arsenicals are also used to some extent and may be encountered by the analyst.

BORDEAUX MIXTURE

Bordeaux mixture is made by the complete precipitation of a copper sulfate solution with lime and the removal of the excess liquid by decantation or filter pressing. It is marketed as a paste and in dry form. Its actual composition is not definitely known, but it probably consists of one or more basic sulfates of copper together with excess calcium hydroxide and incidental impurities. Just what constituent is active fungicidally is also unknown, but the activity of the product is in proportion to its content of copper, which may vary from 7 to 22 per cent, with an average of 12 to 14 per cent, and this constituent is the only one normally determined. However, a scheme for complete analysis is given.

Moisture.—If the product is a powder, determine the moisture simply by drying a small portion at 105° C. to constant weight. In the case of the paste, it is

mixed as thoroughly as possible, and a large portion (about 100 grams) is taken, so that enough dry material will be obtained to serve for the remainder of the analysis. Owing to the alkaline nature of Bordeaux mixture, allowance should be made for any carbon dioxide that may be absorbed during the drying by the scheme described in *Methods of Analysis, A. O. A. C.* The dried material is powdered and used for the remainder of the analysis, but all results are calculated to the original basis.

Copper.—As previously stated, the copper content of Bordeaux mixture is the most important determination on this product. Two methods have been found particularly suitable and have been adopted by the A. O. A. C. One depends on electrolysis of a solution of the sample and the direct weighing of the metallic copper; the other, an adaptation of Low's method, depends on the reduction of the cupric solution with potassium iodide followed by titration of the liberated iodine. Complete directions for both these methods are given in *Methods of Analysis, A. O. A. C.*

Carbon Dioxide.—The carbon dioxide in Bordeaux mixture may be determined by any of the methods used for analysis of lime or limestone. A description of one such method may be found in *Methods of Analysis, A. O. A. C.*

Other Constituents.—These three determinations—moisture, copper and carbon dioxide—are the only ones for which the A. O. A. C. has adopted official methods. The remaining constituents, of which the most important are calcium oxide, magnesium oxide, sulfate, and silica, are not often determined, but when necessary they may be estimated by the following scheme: Dissolve a portion of the sample in hydrochloric acid and evaporate to dehydrate the silica, which is filtered and weighed. Make the filtrate to volume and use one aliquot for the determination of sulfate by precipitation as barium sulfate, and another for determination of calcium as oxalate and magnesium as phosphate.

Little suggestion can be made as to how to calculate a "hypothetical combination." The calcium is probably present as hydroxide, carbonate and sulfate, the magnesia as hydroxide, and the copper as basic sulfate, but no agreement has been reached as to what formula represents the basic sulfate.

COPPER SULFATE AND LIME MIXTURES

In recent years a mixture of copper sulfate monohydrate, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, and lime has been used quite extensively as a dusting substitute for Bordeaux mixture. The mixture consists of approximately equal proportions of the two ingredients and it usually contains about 18 per cent of copper. It may be analyzed exactly like Bordeaux mixture, except that the portions taken for analysis should be varied to suit the different percentages of constituents present.

COMBINATIONS OF BORDEAUX MIXTURE WITH ARSENICAL INSECTICIDES

The desire to lessen the labor of applying fungicides and insecticides separately has led many manufacturers to market combinations of Bordeaux mixture with Paris green, calcium arsenate, or lead arsenate.

In such mixtures the copper, the two forms of arsenic and the water-soluble arsenic are the important constituents and hence the ones most frequently determined. However, methods are given for practically complete analyses.

BORDEAUX-PARIS GREEN

Moisture.—A portion should be dried to constant weight at 105° C.

Total Arsenic.—The simplest method to use is that employing the distillation of the arsenic as arsenious chloride, which can then be titrated with standard iodine or sodium bromate solution. The determination is outlined on pp. 492-3 and described fully in *Methods of Analysis, A. O. A. C.*

Arsenious Oxide.—This constituent may be determined exactly as it is in Paris green, by solution of the sample in hydrochloric acid followed either by direct titration with standard bromate solution or by titration with standard iodine after the addition of excess sodium bicarbonate. Both procedures are described in *Methods of Analysis, A. O. A. C.*

Arsenic Oxide.—Calculate both the total arsenic and the arsenious oxide percentages to the equivalent arsenic oxide values, subtract the smaller from the larger, and consider the difference to be the percentage of arsenic oxide in the sample. The quantity found is usually very small.

Water-Soluble Arsenious Oxide.—This determination is made just as with Paris green, except that a 2 gram sample is used and the aliquot of the extract taken for titration is acidified with hydrochloric acid to destroy calcium hydroxide before the addition of sodium bicarbonate. A description of this method will be found in *Methods of Analysis, A. O. A. C.*

Copper.—Copper may be determined in Bordeaux-Paris green electrolytically, but some provision must be made to remove or oxidize the arsenic, because when in the trivalent state it has a tendency to precipitate along with the copper. Two procedures are open to the analyst. One consists in removing the arsenic by evaporation with hydrobromic and hydrochloric acid and is completely described in *Methods of Analysis, A. O. A. C.* The other consists in dissolving the sample in nitric acid, oxidizing the arsenic with hydrogen peroxide, and maintaining an excess of hydrogen peroxide throughout the electrolysis. It appears that metallic arsenic will not deposit electrolytically directly from an acidified arsenate solution. This method, which is described in *Methods of Analysis, A. O. A. C.*, is preferred because the preparation of the sample is simpler than that in the former method.

Low's titration method, with certain modifications, may also be applied to the determination of copper in Bordeaux-Paris green. Since trivalent arsenic is at least partially oxidized by iodine in dilute acetic acid solution, the iodine liberated in

Low's method would be partially absorbed by the arsenic. The latter should be removed by the A. O. A. C. method.

The remaining constituents of Bordeaux-Paris green mixture are seldom determined, but when necessary they may be estimated in the same way as recommended for Bordeaux mixture alone.

In interpreting the analysis of a Bordeaux-Paris green mixture, the analyst is confronted with the task of deciding what proportion of the copper is present in the form of Paris green and Bordeaux, respectively. Paris green does not always conform to its theoretical analysis, but it is customary to assume that it does. Hence the percentage of Paris green present is figured from the total arsenic (As) present by multiplying by 2.255, and the equivalent copper (per cent As \times .5654) is subtracted from the total copper to obtain that present as Bordeaux mixture.

BORDEAUX MIXTURE WITH CALCIUM ARSENATE

This mixture, which is used extensively as a combined insecticide and fungicide, does not need any detailed treatment from the analytical standpoint. It contains practically the same constituents as Bordeaux mixture with Paris green (except pentavalent arsenic instead of trivalent) and may be handled by the same methods as employed in the case of that product. The proportion of tricalcium arsenate present is to be figured from the total arsenic (As) by multiplying by 2.6556.

BORDEAUX MIXTURE WITH LEAD ARSENATE

This product cannot be analyzed by the methods given for Bordeaux-Paris green because the lead offers complications in the determination of both calcium and copper. A scheme of procedure has been devised, however, by which any mixture of copper fungicides and common arsenical insecticides may be analyzed. This is given in detail in *Methods of Analysis, A. O. A. C.*, and is applicable to a mixture of Bordeaux and lead arsenate. Even the determination of zinc has been considered owing to the possibility of the presence of zinc arsenite. The scheme for the determination of all constituents other than arsenic may be briefly outlined as follows:

Remove the arsenic from a portion of the sample by evaporation with hydrobromic and hydrochloric acids, remove the silica by filtration and precipitate the copper and lead as sulfides. Use the filtrate from these sulfides for determinations of calcium, magnesium and zinc. Digest the mixed sulfides of lead and copper with sulfuric and nitric acids, weigh the lead as sulfate, and determine the copper in the filtrate by electrolysis or some other suitable means.

Total Arsenic.—The distillation as arsenious chloride is the simplest procedure.

Water-Soluble Arsenic.—Determine in the usual way, as previously described, by extracting a 2 gram portion with distilled water for 24 hours at 32° C., filtering, and estimating the arsenic in the filtrate by the Gooch-Browning method. If it is desired to estimate both forms of arsenic, titrate another portion directly for trivalent arsenic, and estimate the pentavalent form by difference.

COPPER CARBONATE

In recent years the problem of protecting crops from certain diseases has been attacked from the angle of disinfecting the seed, to prevent transmitting the disease from one generation to the next. Among the various seed disinfectants used for this purpose the preparation known as copper carbonate has proved very valuable. It is used to the extent of perhaps half a million pounds annually.

Copper carbonate is usually made by the precipitation of a solution of copper sulfate by means of a solution of sodium carbonate. It is not the normal copper carbonate, CuCO_3 , but a basic compound with the copper content normally running between 50 and 55 per cent, and the carbon dioxide content, between 15 and 20 per cent. The composition is usually represented by the formula $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. It also contains small quantities of sulfate, due to the simultaneous precipitation of basic copper sulfate or to the adsorption of sodium sulfate.

The activity of this preparation as a fungicide depends largely on its physical nature since it is necessary that it be divided to an extremely fine state in order that it may come into contact with the spores. No physical standards for the product have been fixed, however, and the analyst is restricted to the chemical examination. The copper is regarded as the important constituent.

Copper.—In preparations consisting of copper carbonate only, determine the copper either by Low's iodide method or by electrolysis. These methods have been described fully under the other copper-containing products. Copper is reported as metallic copper (Cu).

Carbon Dioxide.—Determine by evolution and absorption in any approved train of apparatus, as described on p. 545.

AMMONIACAL SOLUTIONS OF COPPER

Solutions prepared by dissolving copper carbonate or hydroxide in ammonia water or in a solution of ammonium carbonate find limited use as fungicides. They can be analyzed for copper and carbon dioxide by the same methods as used for copper carbonate. The ammonia content may be determined by distillation as follows:

Total Ammonia.—Place a suitable sample in a distilling flask and connect the latter through a Kjeldahl trap with a water-cooled condenser. Add 25 cc. of 5 per cent sodium hydroxide solution to the sample through a dropping funnel and distil into 50 cc. of approximately 0.1 *N* standard acid. When a test with litmus paper shows that all the ammonia has been expelled from the sample, titrate the excess acid in the receiver with standard sodium hydroxide (about 0.1 *N*), using methyl orange or methyl red as indicator. From the quantity of acid used up calculate the percentage of ammonia (NH_3).

The results of the analysis are ordinarily reported as copper (Cu), carbon dioxide (CO_2), and ammonia (NH_3), no attempt being made to calculate the components to a hypothetical combination. The chemistry of the cuprammonium compounds is so complex that it is practically impossible to tell what particular one is present in any specific case.

CHAPTER VII

SULFUR AND ITS COMPOUNDS

Sulfur and some of its compounds are used both as insecticides and fungicides. Elemental sulfur is applied as a dust for the control of mites and fungi on plants and lice on fowls and animals; it is burned in the fumigation of buildings for the destruction of insects and bacteria; and it is also used as a spray in the form of very finely divided sulfur suspended in water.

Several of the polysulfides are important both as insecticides and fungicides. Calcium polysulfide or lime-sulfur is widely used as a dormant spray against scale insects and as a summer spray against fungi. It is also used as a dip against animal parasites. Barium tetrasulfide, sodium polysulfide or "soluble sulfur," and potassium sulfide or "liver of sulfur" are also used to some extent for the same purposes.

Carbon disulfide is widely used as a fumigant for the control of grain weevils, and to a lesser extent to kill rodents in their dens and burrows. It is used in the form of an emulsion as a soil fumigant.

PRODUCTS CONSISTING ESSENTIALLY OF ELEMENTAL SULFUR

Preparation of Sample.—Elemental sulfur, with a purity of 99 per cent or more, is used in the form of powder or fumigating candles. No preparation other than thorough mixing will be needed for powdered sulfur, but the candles should be broken up, ground fine enough to pass a 40-mesh sieve, and mixed thoroughly.

Moisture.—Weigh 2-5 grams in a flat-bottom moisture dish or evaporating dish, dry to constant weight at 100°–105° C., and report percentage loss in weight as moisture.

Non-Volatile Matter.—Weigh 2-5 grams in a porcelain crucible and ignite under a hood until all sulfur is burned off. Weigh the residue and report as percentage of non-volatile residue.

Total Sulfur.—*Extraction Method.*—Weigh 1 or 2 grams of the powdered sample, transfer to a funnel fitted with a dry filter paper and extract with carbon disulfide known to be free from non-volatile residue. Add the solvent in small portions and catch the filtrate in a weighed beaker. Continue the washing until all the sulfur is extracted. Evaporate the carbon disulfide on a steam bath or spontaneously at room temperature, avoiding the proximity of flames. Heat the residue for 15–20 minutes at 100°–105° C. and weigh as elemental sulfur. Samples containing sublimed sulfur are not completely soluble in carbon disulfide and must be analyzed by oxidation, or the sulfur converted to the soluble form by heating.¹

Oxidation in Acid Solution.—Weigh 0.1 gram of sample and transfer to a 400 cc. Pyrex beaker. Place the beaker in a bath of cold water, add 25–30 cc. of fuming nitric acid, cover with a watch-glass, and allow to stand for 10–15 minutes. Remove

¹ *Ind. Eng. Chem. Anal. Ed.*, **2**, 371 (1930).

the beaker to a steam bath and heat for several hours until the sulfur is completely oxidized. (The addition of 1 or 2 cc. of bromine to the nitric acid will hasten the oxidation.) Remove the watch-glass from the beaker and evaporate the acid solution to dryness. Add a few cc. of hydrochloric acid and again evaporate to dryness to destroy nitrates. Take up with 100 cc. of water and 10–15 cc. of dilute hydrochloric acid (1 + 4). Filter if necessary into a 500 cc. beaker, dilute the filtrate and washings to 400 cc., heat to boiling, and add sufficient 10 per cent barium chloride solution to precipitate the sulfate. Add the barium chloride solution drop by drop from a buret, not faster than 1 cc. per minute, with constant stirring. Allow to stand on a steam bath for 1–2 hours, filter, wash with hot water, ignite at the temperature of a Bunsen burner, and weigh as barium sulfate.

From the weight of barium sulfate, calculate the percentage of sulfur in the sample.

Oxidation in Alkaline Solution.—Weigh 0.1 gram of sample and transfer to a 400 cc. Pyrex beaker. Add 10 cc. of 25 per cent sodium hydroxide solution and heat on a steam bath until the sulfur is dissolved. Add 2–3 grams of sodium peroxide dissolved in 50 cc. of water, cover the beaker with a watch-glass and heat on a steam bath, with occasional stirring, until all the sulfur is oxidized to sulfate. Wash off the watch-glass and sides of the beaker, acidify with hydrochloric acid (1 + 4), adding 10–15 cc. of the strong acid in excess, and filter if necessary. (If the addition of the acid causes a precipitate to form, it indicates that the oxidation was incomplete and the determination must be repeated.) From this point proceed as directed under "Oxidation in acid solution" beginning with "dilute the filtrate and washings to 400 cc."

"WETTABLE" SULFUR

This material is composed of very finely ground or precipitated sulfur. It forms a paste with water and usually contains a small quantity of glue, gum, or sodium silicate as a "deflocculator." The preparation mixes readily on the addition of water to make suspensions of spray strength, in which respect it is superior to ordinary powdered sulfur.

Sampling.—Thoroughly mix the entire contents of the package. If the sample is large, preserve a portion in a smaller container sealed to prevent evaporation of water.

Water.—Weigh 50 grams of the thoroughly mixed sample into a flat-bottom crystallizing dish. Dry on a steam bath until most of the water is expelled, transfer to an oven, and dry to constant weight at 100°–105° C., and calculate the loss as "water." Grind the dry sample to a fine powder, mix well, transfer to a sample bottle, and use this dry material for analysis.

Sulfur.—Determine as directed under "Elemental Sulfur" and calculate results to original basis.

Non-Volatile Matter.—Determine as described under "Elemental Sulfur" and calculate results to original basis. The residue may be examined and its nature determined.

SULFUR DUSTING MIXTURES

Since difficulty is encountered in the application of powdered sulfur to plants, lime or other material is added to it in order to improve its dusting qualities. The further combination of such mixtures with insecticides, particularly lead arsenate and calcium arsenate, has become quite common. The mixtures used are of such diversity that it is difficult to formulate methods applicable to all cases; those given are designed for use with mixtures consisting of sulfur and one or more of the following materials: lime, lead arsenate and calcium arsenate.

Sampling.—Use the general method for sampling powders, p. 480.

Sulfur.—Determine by carbon disulfide extraction as described under "Elemental Sulfur," using a 1 gram sample. Keep in mind the fact that sublimed sulfur is not completely soluble in carbon disulfide.

If the sulfur in the sample is not completely soluble, heat the residue at 100°–105° C. to expel the carbon disulfide and oxidize the residual sulfur with nitric acid, as described under "Elemental Sulfur." After the oxidation is complete and the contents of the beaker have been evaporated to dryness with hydrochloric acid to destroy nitrates and dehydrate silica, take up the residue with 25 cc. of dilute hydrochloric acid (1 + 4), and heat to boiling to dissolve the lead chloride and lead and calcium sulfates.

If there is much lead arsenate in the sample, use more acid if necessary to dissolve the residue. Filter the solution as quickly as possible after removal from the flame and immediately wash with boiling water to prevent crystallization of lead chloride on the filter paper. Wash thoroughly with hot water, dilute to 300–400 cc., add 10 grams of ammonium chloride, heat to boiling, precipitate with barium chloride, and determine as barium sulfate, as described under the oxidation methods for elemental sulfur. Make correction for any sulfur originally present as sulfate or other combination.

Total Arsenic Oxide.—Weigh 2 grams of the sample, transfer to a beaker, add 100 cc. of dilute nitric acid (1 + 6), and heat on a steam bath until the materials other than sulfur have dissolved. Cool, transfer to a 200 cc. flask, and make to volume. Filter through a dry filter and determine the arsenic oxide by the Gooch-Browning method, as described under "Lead Arsenate."

Lead Oxide.—Determine by the chromate method as described under "Lead Arsenate," using 0.5–1.0 gram of the sample.

Other Constituents.—Calcium, magnesium, iron and aluminum oxides may be determined by the usual analytical methods for these elements, after the removal of arsenic and lead with hydrobromic acid and hydrogen sulfide as described in *Methods of Analysis, A. O. A. C.*

LIME-SULFUR SOLUTION

Lime-sulfur solution is prepared by heating together sulfur, freshly slaked lime, and water. The mixture is boiled until the reaction is com-

plete and then filtered to remove the insoluble sludge, which is discarded. The solution is an orange-red liquid of 32° - 33° Bé. (sp. gr. 1.283-1.295) and is composed of 30 to 32 per cent of calcium polysulfide (CaS_x , in which x usually lies between 4 and 5), 1.5 to 2.5 per cent of calcium thiosulfate (CaS_2O_3), traces of calcium sulfate and other sulfur compounds, soluble impurities from the lime, and water.

The determinations usually made on this product are specific gravity, total lime, total sulfur, sulfide sulfur, thiosulfate sulfur, and occasionally sulfate sulfur.

Preparation of Sample and General Methods of Analysis.—Mix the sample by shaking and preserve subsamples in tightly stoppered bottles filled to the neck, because lime-sulfur solution decomposes when exposed to the air. For analysis weigh about 10 grams, dilute to a volume of 250 cc. with freshly boiled and cooled water, and thoroughly mix. If the analysis is not to be carried out immediately, preserve the diluted solution in several small bottles that are completely filled and sealed. Determine the specific gravity of the undiluted sample by any convenient means, such as a hydrometer, pycnometer or Westphal balance.

Many methods and modifications have been proposed and studied for the chemical analysis of this product, but only a few need be mentioned here. Those used most generally at this time are the zinc chloride and the iodine titration methods (*Methods of Analysis*, A. O. A. C.). Both of these methods follow the same procedure for the determination of total lime and total sulfur. The lime is determined by adding hydrochloric acid to an aliquot of the diluted solution, evaporating to dryness, taking up the residue with water and a little hydrochloric acid, filtering, and precipitating the lime in the filtrate as calcium oxalate in the usual way.

For the determination of the total sulfur an aliquot of the diluted sample is oxidized with sodium peroxide, acidified with hydrochloric acid, and filtered, and the sulfur is determined by precipitation with barium chloride. In order to prevent contamination of the precipitate with calcium sulfate the solution is made strongly acid with hydrochloric acid before the addition of the barium chloride, after which it is evaporated to dryness and then taken up with hot water and filtered.

Zinc Chloride Method.—Precipitate the sulfide sulfur as a mixture of zinc sulfide and sulfur by means of ammoniacal zinc chloride solution. Filter and wash the mixture, and oxidize the residue with sodium peroxide, then determine the sulfur by precipitation with barium chloride in the same manner as for total sulfur.

Determine the thiosulfate sulfur by titration with iodine after precipitation of the sulfide sulfur with ammoniacal zinc chloride, using a much larger aliquot than for sulfide sulfur and making the precipitation in a volumetric flask. After precipitation make the solution in the flask to volume and filter through a dry filter. Neutralize an aliquot of the filtrate with 0.1 *N* hydrochloric acid and then titrate with standard iodine solution.

Determine sulfate sulfur by precipitation with barium chloride in the solution after titrating the thiosulfate.

Iodine Titration Method.—Titrate an aliquot of the suitably diluted sample with 0.1 *N* iodine until the yellow color just disappears, which gives the "monosulfide equivalent," or calcium combined as polysulfide, the reaction being, theoretically, $\text{CaS}_x + \text{I}_2 = \text{CaI}_2 + \text{S}_x$.

Continue the titration, allowing the iodine to act as its own indicator, until a small drop produces a permanent yellow coloration. The difference between the two titrations gives the thiosulfate sulfur, according to the following reaction: $2\text{CaS}_2\text{O}_3 + \text{I}_2 = \text{CaI}_2 + \text{CaS}_4\text{O}_6$.

After the titration is finished allow the solution to stand for some time to coagulate the sulfur. Filter the solution, dissolve the sulfur in sodium hydroxide, oxidize with sodium peroxide, and determine by precipitation with barium chloride in the usual way. (This represents the sulfide sulfur.)

Determine sulfate sulfur in the filtrate from the precipitated sulfur by precipitation with barium chloride.

These two methods were thoroughly studied before adoption by the A. O. A. C. The results by the zinc chloride method are probably more accurate than those by the iodine titration method. The latter method has the fault that any errors of reading the end point in the titration of the "monosulfide equivalent" affects the results for thiosulfate. The methods are thoroughly discussed by Averitt,¹ Roark,² and Winter.³

Other Methods.—Thompson and Whittier⁴ follow the procedure of the zinc chloride method for the determination of sulfide and thiosulfate sulfur except that cadmium chloride is substituted for zinc chloride in the precipitating reagent. They state that an excess of the reagent must be avoided because cadmium sulfide occludes more of the thiosulfate than does zinc sulfide. They treat another portion of the sample with a solution of potassium cyanide to convert the polysulfides into thiocyanate, and then precipitate the monosulfide sulfur with cadmium chloride exactly as in the determination of sulfide sulfur. The reaction between the polysulfide sulfur and the potassium cyanide may be shown by the following equation: $3\text{KCN} + \text{CaS}_4 = 3\text{KSCN} + \text{CaS}$.

Chapin⁵ has proposed methods for use primarily with diluted solutions of lime-sulfur (containing 1.5 to 2 per cent of sulfide sulfur) such as are used for dipping cattle and sheep. He proposed the determination of "sulfide base" figure, "reaction" figure, "sulfide acid" figure, polysulfide sulfur and thiosulfate sulfur, for all of which he gives titration methods.

¹ *J. Assoc. Official Agr. Chem.*, **1**, 59 (1915).

² *Ibid.*, **76**; **3**, 338 (1920).

³ *Ibid.*, **4**, 142 (1920).

⁴ Delaware Coll. Agr. Expt. Sta. Bull. **105**.

⁵ *J. Ind. Eng. Chem.*, **8**, 151, 339 (1916).

DRY LIME-SULFUR

This product is manufactured and sold in an effort to supply orchardists with an effective substitute for the liquid lime-sulfur, the latter being objectionable from a packing and shipping standpoint due to the large quantity of water it contains.

Dry lime-sulfur is generally manufactured by first preparing a commercial lime-sulfur solution in the usual manner, adding a stabilizing substance (usually cane sugar), and then evaporating to dryness either in vacuo or at atmospheric pressure in the presence of an inert gas. The commercial product contains a relatively large percentage of insoluble matter, consisting chiefly of free sulfur with smaller quantities of calcium sulfite and lime. The average percentage composition of six different brands, as indicated by the analysis of 43 samples from the principal manufacturers, is given by Abbott, Culver and Morgan¹ as follows: Calcium polysulfides 65, calcium thiosulfate 8, free sulfur 10, other ingredients 17.

Sampling and Preparation of Sample.—This product, which is a powder, is usually packed in cans with close fitting covers. When received at the laboratory, sample as described under "Sampling," p. 480, and keep in a tightly stoppered bottle.

The procedure generally followed in the analysis of dry lime-sulfur is to make a water solution of a portion of the sample and then to analyze the solution and residue separately.

Treat 5 grams of the sample in a beaker with successive portions of water at room temperature and decant each time through a filter paper into a 250 cc. volumetric flask until about 200 cc. has been used. Finally transfer the residue to the filter, wash with hot water, cool, and make to volume. Dry the residue at 105° C. for 1-1½ hours and reserve for analysis.

Analysis of Solution.—Proceed exactly as directed under "Lime-sulfur," *Methods of Analysis, A. O. A. C.* The determinations marked with a star are not considered necessary in all cases, and they may be omitted when not desired.

Free Sulfur.—Extract the sulfur from the dried residue with carbon disulfide. Evaporate the carbon disulfide on the steam bath or in a current of air, dry at 105° C. for 15 minutes, weigh the sulfur, and calculate its percentage. (During this determination great care should be taken to avoid open flames.)

***Sulfite Sulfur.**—Expel the carbon disulfide from the residue by exposure to the air or by gently heating and transfer paper and residue to a 250 cc. beaker. Add sufficient water to cover the paper and residue (50-75 cc.), cover the beaker with a watch-glass, and place on a steam bath. Add a small quantity of sodium peroxide measured on the end of a spatula, and heat until all sulfur compounds are oxidized to sulfates, adding more sodium peroxide if necessary. Acidify with hydrochloric acid and make to volume in a 250 cc. flask. Determine the resulting sulfate sulfur

¹ U. S. Dept. Agr. Bull. 1371, p. 7.

in a 100 cc. aliquot by precipitation as barium sulfate and calculate as percentage of sulfite sulfur. Calculate the sulfite sulfur to calcium sulfite (CaSO_3).

***Calcium.**—Determine calcium in a 100 cc. aliquot of the solution, preparation of which was described under "Sulfite Sulfur," by precipitation with ammonium oxalate and subsequent titration or ignition.

***Carbon Dioxide.**—Treat 2 grams of the sample with water, as described under "Preparation of Sample" and determine carbon dioxide in the residue as described under "Bordeaux Mixture." Calcium sulfite may interfere but generally the quantity present is so small that the sulfur dioxide evolved is all absorbed in the sulfuric acid used for drying the carbon dioxide. Otherwise a tube filled with an oxidizing agent such as potassium permanganate or dichromate should be used. Calculate the carbon dioxide to calcium carbonate.

***Calcium Hydroxide.**—After calculating the calcium equivalent to the sulfite sulfur and the carbon dioxide, calculate the remaining calcium from the residue to calcium hydroxide.

***Water (Approximate).**—Remove the sulfur from 2 grams of the original sample with carbon disulfide and dry the residue at 105°C . The total loss in weight is water and sulfur. From this loss subtract the sulfur and calculate the difference as percentage of water.

***Sugars (Sucrose).**—Transfer 5 grams of the original sample to a 250 cc. volumetric flask and shake with 50 cc. of water until the sugar has dissolved. Add 100 cc. of a lead acetate solution containing 250 grams per liter, and allow to stand for 5 minutes with occasional shaking to precipitate the sulfides; then add 50 cc. of a sodium carbonate solution containing 200 grams per liter, allow to stand 5 minutes, make to volume, mix, and filter through a dry fluted filter. Test a portion of the filtrate for sulfides with some of the lead reagent and another portion for lead and calcium with ammonium carbonate solution.

Determine the invert sugar by the Munson and Walker method.¹ Multiply the value for invert sugar found by the factor 0.95 to convert it to sucrose and calculate the percentage of sucrose in the sample.

Other Methods.—Jones² proposes other methods for the analysis of dry lime-sulfur in which the hydrogen sulfide equivalent to the monosulfide of calcium is expelled from the sample with carbonic or hydrochloric acid, absorbed in sodium peroxide solution, and determined as barium sulfate. The sulfur in the evolution flask is filtered off and weighed. This filtrate consists of sulfur already existing in the sample as free sulfur together with that originally present as polysulfide and liberated by the action of the acid. Thiosulfate sulfur is determined by iodine titration in the filtrate from the evolution flask.

The total sulfur is determined by precipitation as barium sulfate after oxidation of a portion of the original sample with sodium peroxide in the same manner as in the official method.

¹ *Methods of Analysis*, A. O. A. C.

² *J. Agr. Research*, **25**, 323 (1923).

Jones makes no attempt to distinguish between the free and polysulfide sulfur. Abbott, Culver and Morgan¹ show that free sulfur has no effect against the San José scale and that the pentasulfide and tetrasulfide are the ingredients in lime-sulfur that are most effective against these insects. In view of these facts it would seem that methods for the analysis of this product which fail to differentiate between polysulfide sulfur and free sulfur are not adequate.

DRY BARIUM-SULFUR PREPARATIONS

The dry barium-sulfur preparations, which are sold for the same purposes as lime-sulfur solution, are of comparatively recent development. Several methods for their preparation have been used, but practically all of those produced at the present time consist simply of a mixture of "black ash" (a crude barium sulfide (BaS) made by heating barium sulfate with coal in a furnace) and sulfur. The product dissolves in water to produce a solution consisting principally of barium polysulfide.

The average percentage composition of nine samples reported by Abbott, Culver and Morgan¹ is as follows: Barium sulfide 38, free sulfur 35, barium thiosulfate 4 and other ingredients 23.

Sampling.—Sample this product and preserve the sample as directed for "Dry Lime-Sulfur."

Free Sulfur.—Place 5 grams of the sample on a hardened filter paper in a short-stemmed funnel and extract the sulfur with successive small portions of carbon disulfide until about 100 cc. has been used. Determine whether all of the free sulfur has been extracted by changing the receiver, extracting with 10 cc. more of the carbon disulfide, and evaporating off the solvent.

Evaporate the carbon disulfide from the extract on a steam bath or in a current of air, dry at 105°C . for 15 minutes, weigh the sulfur, and calculate its percentage. (During this determination great care should be taken to avoid open flames.)

Preparation of Solution.—Expel the carbon disulfide from the residue on the filter and add the residue in small portions to about 100 cc. of water in a 250 cc. beaker with stirring and break up any hard particles. Filter into a 250 cc. volumetric flask, wash the residue thoroughly with hot water, cool, and make the solution to volume.

Non-Volatile Insoluble Residue.—The residue contains barium sulfate, silicious material, and carbonaceous matter. Ignite the residue, weigh, and make qualitative tests for barium sulfate and silicious material. Calculate the percentage and report as non-volatile insoluble material.

¹ U. S. Dept. Agr. Bull. 1371.

Analysis of Solution.—*Barium.*—Transfer 50 cc. of the solution to a 250 cc. beaker, acidify with hydrochloric acid, and heat on the steam bath until the sulfur coagulates, but do not evaporate to dryness. Filter into a 400 cc. beaker, dilute to about 200 cc., precipitate the barium with dilute sulfuric acid, heat on the steam bath for 30 minutes, filter, and wash with hot water. Ignite carefully and heat to constant weight over a Bunsen burner. From the weight of barium sulfate calculate the percentage of barium in the sample.

Total Sulfur.—Dissolve 2–3 grams of sodium peroxide in 50 cc. of cold water in a 250 cc. beaker. Transfer a 10 cc. aliquot of the solution prepared as directed above to this aqueous solution of sodium peroxide, keeping the tip of the pipet constantly just under the surface of the liquid until necessary to raise it for drainage at the end. Use a clean dry pipet for measuring each portion. Cover the beaker with a watch-glass and heat on a steam bath, with occasional stirring, until all the sulfur is oxidized to sulfate (indicated by the disappearance of the yellow color). Wash off the watch-glass and sides of the beaker, acidify with dilute hydrochloric acid (1 + 4), and add 15–20 cc. in excess. Dilute to about 300 cc., heat to boiling, and add 10 cc. of 10 per cent barium chloride solution slowly and with constant stirring. (The barium chloride should be added at such a rate that about 4 minutes is required for running in the necessary quantity. The rate may be regulated by attaching a suitable capillary tip to a buret containing the barium chloride solution.) Boil for a few minutes and allow to stand on a steam bath for 30 minutes. Filter through a quantitative filter, wash free from chlorides, ignite carefully, and heat to constant weight over a Bunsen burner. Calculate the percentage of sulfur from the weight of barium sulfate, using the factor 0.1374.

Sulfide and Thiosulfate Sulfur.—Determine the sulfide and thiosulfate sulfur in the same way as in lime-sulfur solutions, using aliquots of the solution prepared as directed above. Any sulfate sulfur that may have been in the sample will be in the insoluble residue left after the preparation of the solution for analysis.

DRY SODIUM-SULFUR COMPOUNDS

These preparations are generally referred to as “soluble sulfur.” The method most generally used for their manufacture consists in heating or fusing together sulfur and sodium carbonate, or sulfur and caustic soda.

Abbott, Culver and Morgan¹ call attention to the fact that these products are extremely variable in composition. In the samples that they analyzed the sodium polysulfide varied from 2 to 72 per cent, sodium thiosulfate from 8 to 62 per cent, and free sulfur from 0.1 to 20 per cent.

Sampling.—This product is usually received by the analyst as a mixture of fine and lumpy material packed in cans with tightly fitting covers. In sampling break all large lumps and mix thoroughly. Do not attempt to sift the material and avoid long exposure to the air. Preserve the sample in a tightly stoppered bottle.

Preparation of Sample.—Treat 10 grams of the sample in a beaker with 100 cc. of water; stir thoroughly, breaking up the lumps, to dissolve as much material

¹ *Loc cit.*

as possible; and decant through a filter into a 500 cc. volumetric flask. Wash 3 times by decantation, using 50 cc. of water each time, and finally transfer the residue to the filter; wash with hot water until the filtrate is colorless; cool, and make to volume. The residue is free sulfur and other insoluble matter.

Free Sulfur.—Dry the filter and residue at 105° C. Extract the residue with small portions of carbon disulfide, using a total of 50 cc., and evaporate the solvent on a steam bath or in a current of air; dry at 105° C. for 15 minutes, weigh the sulfur, and calculate its percentage. (In making this determination great care should be taken to avoid open flames.)

Non-Volatile Insoluble Matter.—Ignite the filter, weigh the residue, calculate, and report as percentage of non-volatile insoluble residue.

Total Sulfur, Sulfide Sulfur, Thiosulfate Sulfur, and Sulfate Sulfur.—Determine as directed for lime-sulfur solutions, using an aliquot of the solution prepared as directed above.

Sodium.—Transfer 25 cc. of the solution to a 150 cc. beaker, add 10 drops of concentrated sulfuric acid, evaporate as far as possible on a steam bath, and then heat to fuming on a hot plate. Cool, take up with water, filter into a 50 cc. platinum dish, add 1 drop of concentrated sulfuric acid, evaporate to dryness, ignite at the full heat of a Bunsen burner, cool, and weigh as sodium sulfate. From this weight calculate the percentage of sodium in the sample. Prove the absence of other metals by qualitative tests.

Carbon Dioxide.—Dilute 50 cc. of the solution prepared as described above to 150 cc. and add sufficient barium chloride solution to precipitate the carbonates. Place the beaker on the steam bath until the precipitate settles, filter, and wash several times with water. Transfer the paper and precipitate to a carbon dioxide apparatus and determine the carbon dioxide as described under "Bordeaux Mixture."

Chlorides.—Transfer 50 cc. of the solution to a beaker and add sufficient nitric acid to precipitate the sulfur. Heat on a steam bath for a few minutes to coagulate the sulfur and filter. Precipitate the chlorine in the filtrate by adding silver nitrate solution in slight excess. Heat to boiling, protect from the light, allow to stand until the supernatant liquid is clear, filter, and wash. Test the filtrate with silver nitrate to prove complete precipitation. Wash the precipitate on the filter with dilute ammonia to dissolve the silver chloride away from any sulfide which may have accompanied it, receiving the filtrate in a clean beaker. Add a few drops of silver nitrate solution, acidify with nitric acid, heat to boiling, let stand in a dark place until the liquid is clear, filter on a weighed Gooch crucible previously dried at 140° – 150° C., and wash with hot water, testing the filtrate to prove excess of silver nitrate. Dry the silver chloride at 140° – 150° C., cool, and weigh. Calculate and report as percentage of chlorine.

Moisture (Appoximate).—Dry about 3 grams of the sample for 5 hours at 105° C. calculate the percentage loss in weight, and report as moisture.

CARBON DISULFIDE

Carbon disulfide is a clear, highly volatile, inflammable liquid. It has a boiling point of 46° – 47° C. and a sp. gr. at $15^{\circ}/4^{\circ}$ of 1.270–1.272. It is largely used as a fumigant against insects which attack stored grain and

for destroying ants, grubs, and certain other soil insects infesting green-houses, golf courses, and other places. It is also used for killing rodents in their burrows or dens.

The only examination of this product necessary to establish its purity is the determination of its boiling point, specific gravity, and non-volatile residue.

Boiling Point.—Determine the boiling point by any recognized method, taking great care to avoid superheating.

Specific Gravity.—Determine the specific gravity at $15^{\circ}/4'$ by means of a hydrometer, pycnometer, or Westphal balance

Non-Volatile Residue.—Evaporate a 25 cc. aliquot of the sample in an evaporating dish, on a steam bath, or in a current of air, taking care to avoid the proximity of flames. Dry the residue at 105° C. for 15 minutes and weigh. From the weight of the residue and the weight of the sample used (calculated from its specific gravity) calculate the percentage of non-volatile residue.

CARBON DISULFIDE EMULSIONS

Carbon disulfide emulsions are now used to a considerable extent as soil fumigants, and they have been most widely used against the grubs of the Japanese beetle. Mason¹ gives the following formula for the preparation of an emulsion of this type: (One part by volume of cold-water-soluble resin-fish-oil soap, 3 parts of water, and 10 parts of carbon disulfide.

Fleming² gives the following formula for a nonstratifying carbon disulfide emulsion: 13.5 grams of potassium hydroxide in sufficient alcohol to make 193 cc., 77 cc. of oleic acid, 700 cc. of carbon disulfide, and 30 cc. of cottonseed oil.

Sampling.—Sample this product by the method for sampling emulsions, given on p. 479, and preserve the sample in an air-tight container.

Carbon Disulfide.—Fisher³ recommends the following method, which is a modification of the method of Weiss.⁴

Weigh a glass-stoppered 100 cc. volumetric flask containing 40 cc. of 8 per cent alcoholic potassium hydroxide, add about 2 grams of emulsion, stopper, and reweigh to determine the exact weight of the emulsion added. Make the mixture to volume with 95 per cent alcohol at 20° C., mix well, pipet out a 5 cc. aliquot, and add to a mixture of 50 cc. of water, 50 cc. of 3 per cent hydrogen peroxide, and 10 cc. of 10 per cent potassium hydroxide solution in a beaker. Heat on a steam bath for 1 hour, acidify with hydrochloric acid, filter, heat the filtrate to boiling,

¹ *Spraying, Dusting and Fumigating of Plants*, The MacMillan Company, 1928, p. 250.

² *Ind. Eng. Chem.*, **17**, 1087 (1925).

³ *Ibid.*, **19**, 1201 (1927).

⁴ *J. Ind. Eng. Chem.*, **1**, 604 (1909).

and add 10 cc. of 10 per cent barium chloride solution drop by drop. Allow to stand overnight, filter the barium sulfate on an ashless filter paper, wash with hot water, and carefully ignite in a platinum crucible to constant weight. Run a blank determination on the reagents and make the proper correction. From this corrected weight of barium sulfate calculate the percentage of carbon disulfide, using the factor 0.16306.

Other methods for determining carbon disulfide have been studied by Spielman and Jones.¹ The methods tested by them included oxidation in alkaline solution with bromine and subsequent precipitation and determination as barium sulfate; formation and estimation of xanthate; and precipitation by phenylhydrazine phenylsulfocarbazine.

Fatty and Resin Anhydrides.—Weigh about 20 grams of the sample in a beaker and heat on a steam bath until the carbon disulfide is expelled. Dissolve the residue in hot water, transfer to a separatory funnel, acidify with dilute sulfuric acid, and extract several times with ether. Wash the ether extracts once with water, transfer them to a weighed beaker, evaporate on a steam bath, dry for 30 minutes at 105° C., and weigh. From this weight calculate the percentage of fatty and resin anhydrides, using the factor 0.97.

If desired the resin anhydrides may be separated and determined by the Twitchell method² or the Wolff method.³

Sodium or Potassium Oxide.—Weigh 5 to 10 grams of the emulsion in an evaporating dish and heat on a steam bath until the carbon disulfide and water are expelled. Ignite the residue over a Bunsen burner until well charred, leach the residue with water, filter, and wash several times with water. Ash the residue, take up with water, and filter into the beaker used to receive the first filtrate; wash with water and titrate the filtrate with standard acid. Make a qualitative flame test for sodium and potassium. If it is evident that one or the other largely predominates calculate the titration to sodium or potassium oxide as the case may be. This method is sufficiently accurate for most purposes. However, if a more exact analysis is desired, the alkalies may be determined by weighing the combined chlorides or sulfates in the usual way and separating the potassium as potassium platonic chloride.

Alcohol.—Weigh 20 to 25 grams of the sample into a separatory funnel, acidify with dilute sulfuric acid, and extract several times with petroleum ether to remove the carbon disulfide and fatty and resin acids. Wash the petroleum ether extracts once with water. Transfer the aqueous solution and washings to a distilling flask, distil nearly 100 cc. into a 100 cc. volumetric flask, and make to volume. Determine the specific gravity of the distillate at 20°/4° C., ascertain the corresponding alcohol content in grams per 100 cc. of distillate from the alcohol table, *Methods of Analysis*, A. O. A. C., and calculate the percentage by weight of alcohol in the sample.

Water.—Subtract the sum of the other constituents from 100 and report the difference as percentage of water.

¹ *J. Soc. Chem. Ind.*, **38**, 185 T (1919).

² *Ibid.*, **10**, 804 (1891).

³ *J. Ind. Eng. Chem.*, **14**, 1161 (1922).

CHAPTER VIII

FLUORINE COMPOUNDS

It has long been recognized that the compounds of fluorine have toxic properties, and it is natural that they should have been tried as insecticides. Sodium fluoride has been used as a household remedy against roaches and ants for many years, and recently other fluorine compounds, such as sodium silicofluoride, have been recommended and used as dusts for control of the Mexican bean beetle and other insects.

The fluorides of commerce have their origin in the by-products of the phosphate industry. During the digestion of the phosphate rock with sulfuric acid the fluorine contained as apatite, etc., is expelled as hydrogen fluoride and silicon tetrafluoride. These gases are absorbed in water and yield solutions of hydrofluoric and hydrofluosilicic acids. From these acids the corresponding sodium salts are made by interaction with sodium carbonate.

The analysis of compounds of fluorine offers considerable difficulty. The principal insoluble compound which it forms, calcium fluoride, is ordinarily gelatinous and hard to handle, and the volumetric processes are usually disturbed by slight changes in conditions. Further, fluorine forms complexes with numerous other elements, notably boron, iron and aluminum, and those elements therefore interfere with the fluorine determination.

Qualitative Tests for Fluorine.—Two characteristic properties of fluorine upon which its detection is based are the etching action of hydrofluoric acid on glass and the volatility of silicon tetrafluoride. In general, a product suspected of containing fluoride may be tested for that element as follows:

Place a portion of the sample in a small platinum dish or crucible, mix with it some concentrated sulfuric acid, and cover the dish or crucible with a glass plate that has been waxed and had some lines or design scratched through the wax (a gummed label may also be used). Heat the dish gently, and after some time remove the glass, clean, and examine for an etching of the design. Such etching is conclusive evidence of fluorine.

If no etching is obtained, however, the evidence for lack of fluorine is not so conclusive, since in the presence of silica all the fluorine may form silicon tetrafluoride (SiF_4), which is volatile but which does not act on glass in the absence of moisture. To guard against this possibility the above test is modified by replacing the waxed glass by a watch-glass that has a drop of water hanging from underside. Some of the silicon tetrafluoride that is formed then reacts with the water and deposits gelatinous silica, which is found by later examination.

Since this test is not easily recognized, there may be doubt about the result when the percentage of fluorine is quite low. In such case, proceed as follows: Put 20 grams of sample in a 200 cc. side-neck distilling flask, add 1 or 2 grams of powdered silica, cover it with concentrated sulfuric acid, dip the side-neck tube into a test tube containing water, and heat the flask gently. The appearance of gelatinous silica in the test tube indicates fluorine. If additional evidence is desired, make the water from the test tube slightly alkaline with ammonium hydroxide (whereby more silica may separate), filter, and add a calcium salt. This will precipitate calcium fluoride, which may be filtered off and tested by the etching test described above. In this way it is possible to detect less than 0.1 per cent of sodium fluoride in a sample.

Total Fluorine.—*Volatilization Method.*—The test just described is the basis of a quantitative method of wide applicability. By working in a system kept absolutely dry it is possible to drive off all fluorine as silicon tetrafluoride, which is then absorbed in water and estimated gravimetrically or volumetrically. This method was first proposed by Fresenius, and since his time has been studied by many investigators, some of whom have obtained entirely satisfactory results while others have failed to recover all the fluorine. The most recent detailed study of the conditions necessary has been made by Reynolds, Ross and Jacob.¹ They report that they could recover only 92–94 per cent of the fluorine in a sample of calcium fluoride despite all precautions. Nevertheless it is believed that the method is worth while when applied to very complicated mixtures. It is unfortunate that the method gives inaccurate results in the presence of borax, since that is a very common constituent of the roach powders in which sodium fluoride is largely used.

Calcium Fluoride Precipitation Method.—Another method of general applicability and perhaps of equal importance depends upon fusion of the sample with sodium carbonate and silica with subsequent solution, removal of silica, and precipitation of the fluorine as insoluble calcium fluoride, which is then ignited and weighed. This method, which should be used when borax is present, may be carried out as follows: Mix 0.5–1.0 gram of sample with 1 gram of powdered silica and 5 grams each of sodium carbonate and potassium carbonate. Heat this mixture gradually until it first melts to a thin liquid, then stiffens to a paste and ceases to evolve carbon dioxide. Dissolve the cooled melt in water and filter. Add 5 grams of ammonium carbonate to the filtrate, boil for 5 minutes, and allow to stand overnight. Filter and wash with ammonium carbonate solution. Evaporate the filtrate to dryness, take up the residue in a little water, and add dilute hydrochloric acid until the solution is neutral to phenolphthalein. Boil, and the color will return. Cool, and discharge the color again. Repeat this cycle until it requires only 1–2 cc. of 2 *N* hydrochloric acid to discharge the color. Add 5 cc. of a saturated solution of zinc oxide in concentrated ammonium hydroxide, and boil until the ammonia is completely expelled. Filter the precipitate of zinc silicate and zinc oxide, and wash with water. Neutralize the filtrate, add 1 cc. of 2 *N* sodium carbonate solution and then sufficient calcium chloride solution completely to precipitate the fluoride and excess carbonate, and then 2–3 cc. excess. Filter and wash, transfer the bulk of the residue to a platinum dish, burn the paper separately, adding the ash to the dish, and ignite. Cool, add an excess of dilute acetic acid, and evaporate to dryness on the steam bath.

¹ *J. Assoc. Official Agr. Chem.*, **11**, 225, 237 (1928).

Take up the residue in water, filter, and wash to remove the calcium acetate. Filter, dry, and ignite the residue of calcium fluoride. Calculate the percentage of fluorine in the sample. Check the purity of the final residue of calcium fluoride by fuming it with concentrated sulfuric acid, igniting, and weighing the calcium sulfate formed

This method gives the total fluorine in the sample, but it gives no indication of the form in which it is present.

In many insecticides containing fluorine, especially roach powders, the only fluorine compounds present are water-soluble sodium salts, and it is possible to use simpler methods for their analysis. Frequently ordinary commercial sodium fluoride is simply mixed with pyrethrum powder, starch, or other ingredient, and at times it is sold unmixed. This makes the analysis of commercial sodium fluoride of considerable importance.

SODIUM FLUORIDE

Commercial sodium fluoride is usually made by the neutralization of hydrofluoric acid with sodium carbonate. Commercial hydrofluoric acid almost always contains hydrofluosilicic acid, so that the finished sodium fluoride will contain one or more other substances, depending on conditions of neutralization. When alkali is added to hydrofluosilicic acid, the first effect is to neutralize the acid and produce sodium silicofluoride. If the neutralization is carried no farther than this, the finished sodium fluoride will contain sodium silicofluoride. If not neutralized quite this far, there may even be some sodium bifluoride formed. If, however, the addition of sodium carbonate is carried to the point at which the solution, when hot, is alkaline to phenolphthalein, all the bifluoride will be converted to normal fluoride, and the silicofluoride will also be converted to normal fluoride mixed with amorphous silica. If the product is not washed thoroughly it will also contain sodium carbonate. Thus in general, commercial sodium fluoride will tend to consist of one of the two mixtures—

A	B
Sodium bifluoride	Sodium fluoride
Sodium silicofluoride	Silica
Sodium fluoride	Sodium carbonate

from either of which the silicon containing compound may be absent owing to the use of high-grade hydrofluoric acid. However, all these compounds

could be present in one mixture if products of type A and B were mixed dry.

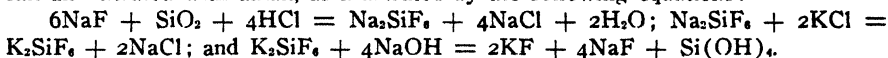
No scheme of analysis is now available whereby all of the 5 components mentioned can be directly determined when present in the same sample. The reaction between bifluorides and carbonates is so rapid that no solution process will distinguish between them. However, a fairly accurate idea of the composition of such a mixture could be obtained indirectly from a complete analysis for the separate elements.

Qualitative Tests.—Cover a portion of sample with 50 per cent alcohol and add a few drops of phenolphthalein solution. An alkaline reaction signifies the presence of sodium carbonate and hence a mixture of type B. Acidity of an aqueous solution to methyl orange signifies the presence of bifluoride and hence a mixture of the type A.

GENERAL METHODS FOR EITHER A OR B

Total Sodium.—Weigh out a 1 gram sample into a platinum dish, cover with 3 cc. of concentrated sulfuric acid, and fume to dryness on a hot plate or over a Bunsen burner. Take up the residue in a little water, and add a pinch of calcium oxide. Filter off any precipitate that forms and precipitate the excess calcium by the addition of a few drops of ammonium oxalate and ammonia. Filter, acidify the filtrate with sulfuric acid, and evaporate as far as possible on the steam bath. Then fume off the excess sulfuric acid, ignite to constant weight, and weigh the sulfates. Calculate to sodium (Na) unless a flame test shows potassium, in which case determine the potassium by one of the usual gravimetric procedures or determine the sulfate radicle and calculate the percentage of potassium present.

Total Fluorine.—*Traver's Method.*—The following method depends upon the fact that in acid solution sodium fluoride combines rapidly and completely with silica to form sodium silicofluoride, which is then precipitated with a potassium salt and titrated with alkali, as illustrated by the following equations:



REAGENTS

(a) *Alcoholic potassium chloride solution.*—Dissolve 60 grams of potassium chloride in 400 cc. of recently boiled and cooled distilled water, and add 400 cc. of neutral 95 per cent ethyl alcohol.

(b) *0.2 N sodium hydroxide solution.*—Prepare an approximately 0.2 N solution of sodium hydroxide in some way which will assure the absence of carbonate. Standardize it against Bureau of Standards benzoic acid or some other suitable comparison material.

DETERMINATION

Treat 0.5 gram of sample in a small beaker with 20–25 cc. of water, add 0.5 gram of finely divided silica (powdered silica gel serves very well) and a few drops

of methyl orange. Add concentrated hydrochloric acid drop by drop until the solution assumes a permanent pink color, after which add 0.5 cc. in excess. Heat just to boiling, cool to room temperature, add 4 grams of solid potassium chloride, and stir until the latter dissolves. Next add 25 cc. of 95 per cent ethyl alcohol, stir, and let stand for 1 hour. Filter under suction and wash with the alcoholic potassium chloride reagent. Transfer the filter and residue to a beaker; add 100 cc. of recently boiled water; heat; and titrate while heating with the standard sodium hydroxide solution, using phenolphthalein indicator. Finish the titration with the solution actively boiling. Calculate the percentage of fluorine on the basis that 1 cc. of 0.2 *N* sodium hydroxide is equivalent to 0.005700 gram of fluorine (F).

Total Silica.

REAGENT

Add excess of zinc oxide to concentrated ammonium hydroxide solution, and shake well for some time. Filter out the undissolved zinc oxide and preserve the solution.

DETERMINATION

Weigh 1 gram of the sample in a platinum dish, cover with 50 cc. of distilled water, add a few drops of bromthymol blue indicator, begin to heat, and add ammonia drop by drop to keep the reaction just alkaline, as shown by a blue color. Boil for several minutes, then add 5 cc. of the ammoniacal zinc reagent. This will precipitate the silica as zinc silicate, which flocculates well, and can be filtered on a Whatman No. 41 filter paper. Wash the precipitate with the reagent to assure complete removal of fluorine. Then ash the filter and contents at a low temperature, treat the ash with hydrochloric acid, evaporate to dryness, and bake in an oven for several hours to render the silica insoluble. Take up in dilute hydrochloric acid, filter, ignite before the blast lamp to constant weight, and weigh as silica (SiO_2). If this percentage of silica exceeds that calculated from the silicofluoride content, regard the difference as silica present as such or as silicate.

Sulfate.—The silicofluoride radicle resembles in some respects the sulfate radicle. Thus it forms an insoluble salt with barium, and makes impossible the determination of sulfates in the usual manner without the previous removal of silicofluorides.

Despite the fact that hydrofluosilicic acid is completely volatile from its aqueous solutions on the steam bath, sodium silicofluoride cannot be easily changed to chloride by evaporation with hydrochloric acid. Hence, if it is desired to estimate the sulfates in a sample containing silicofluoride, it is necessary first to convert the latter to fluoride, remove the fluoride with a calcium salt, and estimate the sulfate in the filtrate. This method may be carried out as follows:

Weigh a 2 gram portion of the sample, cover it with 100 cc. of water in a 250 cc. beaker, and add solid sodium carbonate until the solution persists alkaline to phenolphthalein. Boil for 5 minutes, adding a little more carbonate if necessary to keep alkaline. Cool, and transfer contents of beaker to a 250 cc. volumetric flask. Add a concentrated solution of calcium chloride until the fluoride and carbonate ions are completely precipitated. Make to volume, and either allow to settle or filter through a dry filter. Take a 100 cc. aliquot for the determination of sulfur trioxide in the usual manner, by precipitation as barium sulfate.

METHODS FOR MIXTURE A

Total Fluorine.—Determine by Traver's method, as described on p. 530.

Fluorine Present as Silicofluoride.

REAGENTS

(a) *Alcoholic potassium chloride solution.*—Prepare as directed under "Total Fluorine," p. 530.

(b) *Standard sodium hydroxide solution.*—Prepare an approximately 0.2 *N* solution as described under "Total Fluorine," p. 530.

(c) *Sodium carbonate.*—Finely powdered anhydrous sodium carbonate.

DETERMINATION

This method is practically the same as the Traver's method for total fluorine, except that no silica is added and precautions are taken to prevent the formation of additional silicofluoride from any silica present in the sample.

Weigh 1 gram of the sample into a platinum dish, add 0.5 gram of the finely powdered sodium carbonate, cover with 50 cc. of the alcoholic potassium chloride reagent, and stir well until it is certain that all the sodium carbonate is dissolved. Filter with suction, wash with the alcoholic potassium chloride reagent until the wash liquid is not alkaline to phenolphthalein, and finish the determination as described under "Total Fluorine." Calculate the percentage of sodium silicofluoride on the basis that each cc. of 0.2 *N* sodium hydroxide is equivalent to 0.009403 gram of sodium fluosilicate.

Fluorine Present as Bifluoride.—Weigh accurately 1 gram of the sample into a 100 cc. platinum dish, cover with 50 cc. of recently boiled distilled water, add a few drops of phenolphthalein indicator, and titrate with 0.2 *N* sodium hydroxide solution free from carbonate. When the fading of the color becomes sluggish, heat the dish and contents while titrating, and finish the titration after the solution has begun boiling. The titration is equivalent to the sum of the bifluoride and silicofluoride according to the following equations: $\text{NaHF}_2 + \text{NaOH} = \text{NaF} + \text{H}_2\text{O}$; and $\text{Na}_2\text{SiF}_6 + 4\text{NaOH} = 6\text{NaF} + \text{SiO}_2 + \text{H}_2\text{O}$.

Each cc. of 0.2 *N* alkali is equivalent to 0.012401 gram of sodium bifluoride (NaHF_2). Calculate the titration to percentage of sodium bifluoride on this basis, and subtract from the result 1.3190 times the percentage of sodium silicofluoride to get the percentage of sodium bifluoride actually present.

Total Sodium.—Determine by method already described, p. 530.

METHODS FOR MIXTURE B

Total Sodium.—Determine as described on p. 530.

Total Fluorine.—Determine by Traver's method as described on p. 530.

Total Silica.—Determine as described on p. 531.

Carbon Dioxide.—Estimate the sodium carbonate present in mixtures of this type by dissolving a sample in water and titrating with standard acid to the phenolphthalein end point, or if preferable to determine it by evolution and absorption of carbon dioxide, use the following procedure:

Put a suitable weight of sample into the evolution flask of any good carbon dioxide apparatus, add $\frac{1}{2}$ its weight of powdered silica (preferably powdered silica gel), and determine the carbon dioxide in the usual manner, as described in *Methods of Analysis, A. O. A. C.* The silica serves to convert all the fluorine present into silicofluoride, and thus not only to render it less volatile, but also to protect the evolution flask against severe etching.

The carbon dioxide is ordinarily present in sodium fluoride samples as sodium carbonate, but samples have been encountered in which bicarbonate was also undoubtedly present. In such cases it is necessary to use both evolution and titration methods, and deduce the relative proportions of carbonate and bicarbonate from the results obtained.

SODIUM BIFLUORIDE AND SODIUM SILICOFLUORIDE

Besides being present as impurities in many samples of commercial sodium fluoride, both of these compounds are used to a limited extent as insecticides. Since each may contain some of the other, and both may contain sodium fluoride, they should be analyzed by the methods given for sodium fluoride, with changes in the size of sample taken consistent with the changes in the relative proportions of the various forms of fluorine.

CALCIUM FLUOSILICATE COMPOUND

The only fluorine product other than the compounds of sodium that has been used to any extent is that known as "calcium fluosilicate compound." This is usually very impure, in fact it normally contains fluorine equivalent to about 20 per cent calcium silicofluoride, mixed with calcium phosphate, calcium sulfate, and other compounds. Its complete analysis is quite lengthy, and since it is practically impossible to determine the various forms of fluorine the only important determination is that of total fluorine.

The total fluorine in this type of sample is without doubt most easily estimated by the method previously described which utilizes the volatilization of silicon tetrafluoride.

CHAPTER IX

HYPOCHLORITES AND OTHER CHLORINE COMPOUNDS

Hypochlorites have been used for a long time for bleaching purposes and disinfection. The manufacture of potassium hypochlorite was established by Berthollet, at the Javel works, in 1789, and its use was shortly thereafter advocated as a disinfectant.

The substitution of sodium for potassium in the preparation of Javel water was later suggested by Labarraque, and since then sodium hypochlorite has been more commonly used.

Bleaching powder or chlorinated lime was made by Tennant, who took out a patent for its manufacture in 1798. The use of the chloramines, suggested by Dakin, is of comparatively recent introduction.

CHLORINATED LIME

Chlorinated lime is made by passing chlorine over moist slaked lime, the whole mass being kept well mixed until the absorption of gas is complete. Its composition has not been definitely determined, but it is generally considered that the principal constituent is calcium oxychloride (CaOCl_2), which is accompanied by calcium chloride and free lime in varying quantities. The activity of chlorinated lime is proportional to its "available chlorine" content. This has been defined as the whole quantity of free chlorine that becomes available when the product is decomposed by strong acid. Despite the term "available chlorine," the activity of chlorinated lime as a germicide is commonly considered to depend on its oxidizing and not on its chlorinating power.

Generally the determination of the available chlorine is all that is required.

Sampling.—This product, which is a powder, is usually packed in cans with close-fitting covers. When received at the laboratory, subsample as described under "Sampling," p. 480, without attempting to sift the material. Preserve the subsamples in tightly sealed glass jars or bottles.

Available Chlorine.—*Sodium Arsenite Titration Method.*

REAGENTS

(a) 0.1 *N* sodium arsenite solution.—Use pure resublimed arsenious oxide, which has been dried to constant weight at 105° C. Dissolve exactly 4.948 grams of this pure arsenious oxide in 250-300 cc. of distilled water in which has been dis-

solved 10 grams of anhydrous sodium carbonate. In order to hasten the solution heat the mixture and stir thoroughly, but avoid extended boiling. When all the arsenious oxide is dissolved, indicated by a clear solution, cool and make to volume in a liter volumetric flask. The solution should need no further standardization, but if desired check against standard iodine solution, using starch solution as an indicator.

(b) *Starch-iodide paper*.—Saturate strips of filter paper in a starch-iodide solution prepared as follows: Mix about 1 gram of finely powdered potato starch with cold water to a thin paste, pour into about 100 cc. of boiling water with constant stirring, immediately discontinue heating, and add 10 cc. of a 1 per cent solution of potassium iodide. (The paper should be damp during use.)

DETERMINATION

Weigh 10 grams of the thoroughly mixed sample into a porcelain mortar, add 30–40 cc. of water, and triturate until a smooth cream is obtained. Add more water, stir well with the pestle, and allow the insoluble residue to settle for a few moments. Pour off into a liter volumetric flask, add more water, and again thoroughly triturate the sample and pour off as before. Repeat the operation until all the material has been transferred to the flask. Rinse the mortar and pestle, catch the wash water in the flask, dilute the solution to the mark, and mix. Without allowing the material to settle, pipet a 50 cc. aliquot into a 200 cc. Erlenmeyer flask and titrate with the 0.1 *N* sodium arsenite solution, using starch-iodide paper as an outside indicator. From the number of cc. of sodium arsenite solution used calculate the percentage of available chlorine in the sample, on the basis that 1 cc. of 0.1 *N* $\text{As}_2\text{O}_3 = 0.003546$ gram of available chlorine.

Thiosulfate Titration Method

REAGENTS

(a) *Potassium iodide solution*.—Dissolve 16.5 grams of potassium iodide in water and dilute to 100 cc.

(b) *0.1 *N* thiosulfate solution*.—Prepare by dissolving 26 grams of crystallized sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in recently boiled and cooled water, filter, and dilute to 1 liter with recently boiled and cooled water. Standardize against a standard iodine solution, using starch solution as indicator.

DETERMINATION

Prepare a solution of 10 grams of the sample as described under the sodium arsenite method, and, without allowing the material to settle, pipet a 50 cc. aliquot into a 200 cc. Erlenmeyer flask, and add an excess of the potassium iodide solution. Dilute to about 100 cc.; acidify with acetic acid, adding an excess of 2–4 cc. of 50 per cent acid for each 25 cc. of solution; and titrate the liberated iodine with the 0.1 *N* thiosulfate solution. As an indicator add starch solution toward the end of the titration. From the number of cubic centimeters of thiosulfate used calculate the percentage of available chlorine on the basis that 1 cc. of 0.1 *N* thiosulfate equals 0.003546 gram of available chlorine.

References: R. C. Griffin, *Technical Methods of Analysis*, p. 413; F. Sutton, *A Systematic Handbook of Volumetric Analysis*, 11th ed., p. 186; S. Ochi, *J. Chem. Ind. (Japan)*, **26**, 185-90 (1923).

Chloride Chlorine.—In the determination of chloride chlorine in chlorinated lime no part of the chlorine of the compound, calcium oxychloride $\text{Ca} \begin{array}{l} \text{Cl} \\ \diagup \quad \diagdown \\ \text{OCl} \end{array}$, is considered as chloride chlorine.

REAGENT

0.1 N silver nitrate solution.—Dissolve 17 grams of silver nitrate in 1 liter of water and standardize against pure sodium chloride by titration, using chromate indicator, or gravimetrically by weighing the chloride.

DETERMINATION

To the solution which has been titrated for available chlorine by the sodium arsenite method as previously described, add a slight excess of nitric acid, neutralize the solution with calcium carbonate, and titrate with 0.1 N silver nitrate, using potassium chromate or the sodium arsenate formed in the solution as indicator. Run a blank determination on the reagents and make correction for any chlorine found. From the corrected titration calculate the percentage of chlorine. From this value subtract the percentage of available chlorine. The difference is the percentage of chloride chlorine.

References: George Lunge, *The Manufacture of Sulfuric Acid and Alkali*, 3rd ed., vol. 3, pp. 570-602; U. S. Dept. Agr. Bull. **1389**, p. 5.

Total Chlorine.¹—Transfer a 50 cc. aliquot of the solution prepared for the determination of available chlorine to a 200 cc. Erlenmeyer flask, add an excess of sulfurous acid, heat the mixture to boiling to reduce chlorates, and expel the excess of sulfurous acid. Add 2 or 3 drops of nitric acid to insure complete removal of the sulfurous acid. Cool the solution; neutralize with calcium carbonate; and titrate with silver nitrate, using potassium chromate as indicator. From this titration calculate the percentage of total chlorine in the sample. The difference between this value and the sum of the percentage of chloride chlorine and the percentage of available chlorine is the chlorine existing in the sample in a higher oxidized form. It may be regarded as chlorate chlorine.

Carbon Dioxide.¹

APPARATUS

The following apparatus, Fig. 3, is used for the determination of carbon dioxide in the chlorinated lime.

An evolution flask, A, to which is attached a dropping funnel, C, protected by a tube, B, containing soda lime, is connected to a Kjeldahl distilling trap, D, which in turn is connected to two wash bottles, E, containing glass beads and potassium

¹ U. S. Dept. Agr. Bull. **1389**, p. 6.

iodide solution. The train ends with a Meyer absorption tube, F, containing 0.1 *N* barium hydroxide solution.

DETERMINATION

Weigh 5 grams of the sample into the evolution flask and attach to the rest of the apparatus by means of the stopper carrying the Kjeldahl distilling trap and the dropping funnel with its guard tube. Place 50 cc. of 0.1 *N* barium hydroxide solution in the Meyer tube, and then add 50 cc. of hydrogen peroxide solution through the dropping funnel into the evolution flask. After the action due to the hydrogen peroxide has ceased, add 30 cc. of dilute hydrochloric acid (1 + 3) and draw air

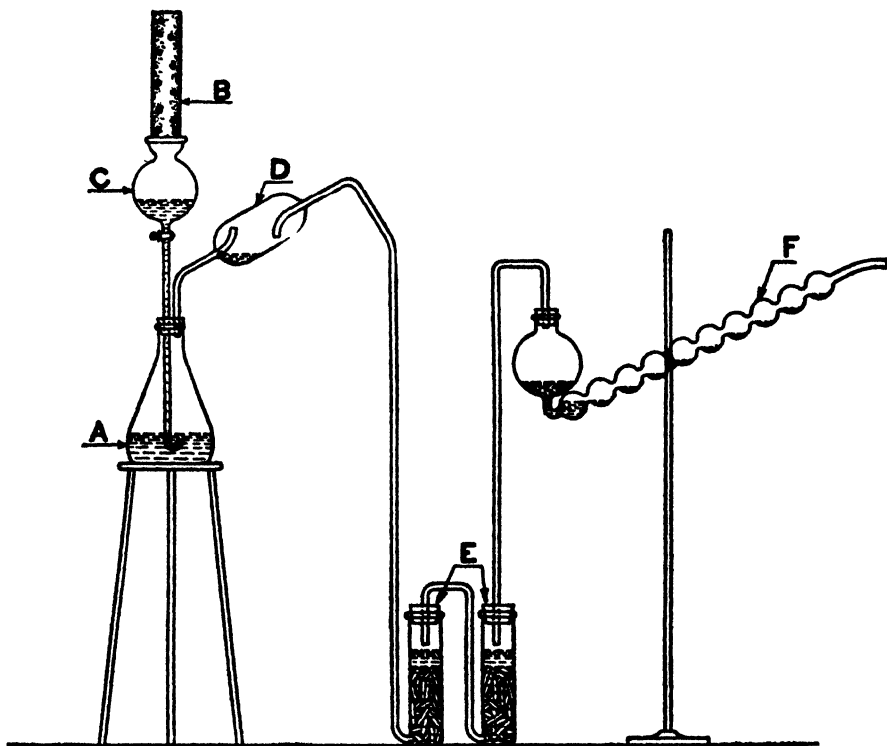


FIG. 3.—Apparatus for Determination of Carbon Dioxide.

slowly through the apparatus. The evolved gases will be freed from chlorine by the potassium iodide in the wash bottles, and the carbon dioxide will be absorbed in the standard barium hydroxide in the Meyer tube. Draw the air through the apparatus for 20 minutes, disconnect the Meyer tube, and pour its contents into a 500 cc. Erlenmeyer flask. Thoroughly wash the Meyer tube and add the washings to the contents of the flask. Titrate the solution without filtering off the precipitated

carbonate, using 0.1 *N* hydrochloric acid with phenolphthalein as an indicator. From the number of cubic centimeters of barium hydroxide solution used calculate the percentage of carbon dioxide, on the basis that 1 cc. of 0.1 *N* barium hydroxide is equivalent to 0.002200 gram of CO_2 .

Calcium, Magnesium, Iron, Aluminum and Silica may be determined by the following scheme which is also given in Bull. 1389.

To 2 grams of the sample in water, in a 250 cc. beaker, add 25 cc. of strong hydrochloric acid (sp. gr. 1.18) and 50 cc. of 3 per cent hydrogen peroxide solution. Evaporate this solution on a steam bath, bake on a hot plate for thirty minutes to dehydrate silica, take up in dilute hydrochloric acid (1 + 9), and filter off the silica. Ignite the precipitate and weigh as silica (SiO_2).

Add ammonia in slight excess to the filtrate and washings, and boil the solution until the odor of ammonia is barely perceptible. Filter the combined hydroxide of iron and aluminum, and collect the filtrate and washings in a 250 cc. volumetric flask. Ignite the precipitate and weigh as iron and aluminum oxides (R_2O_3).

Dilute the filtrate to the mark, mix, and precipitate the calcium in the usual manner with ammonium oxalate, using a 50 cc. aliquot and reprecipitating. Dissolve the precipitate in dilute sulfuric acid and titrate with 0.2 *N* potassium permanganate. Report the result as calcium oxide (CaO). Determine magnesium in the combined filtrate and washings from the calcium determination by precipitating with disodium phosphate solution, igniting, and weighing as magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

SODIUM HYPOCHLORITE SOLUTIONS

Sodium hypochlorite solutions are made by the electrolysis of solutions of sodium chloride; by interaction between chlorinated lime and solutions of sodium carbonate; or by passing chlorine through solutions of sodium hydroxide. This product has come into very extensive use during the past few years as a disinfectant, particularly in the dairy industry, where it has displaced steam to a large extent in the disinfection of milk bottles, cans and other dairy equipment.

It has been claimed by Justin-Mueller¹ that the chemical behavior of the alkaline hypochlorites is best explained by considering them as chemical compounds of the type $\text{ROCl} \cdot \text{RCl}$ or R_2OCl_2 , similar to chlorinated lime. However, they are more generally regarded as being true hypochlorites with the formula ROCl .

Because sodium hypochlorite solutions occur in commerce in varying strengths, the quantity of sample to be taken for analysis cannot be definitely stated. The following methods are based on a sodium hypochlorite content of approximately 5 per cent. For samples containing a different proportion of sodium hypochlorite the quantity of sample used should be varied accordingly.

¹ *J. Pharm. Chim.*, 20, 113 (1919).

Specific Gravity.—Determine the specific gravity at $20^{\circ}/4^{\circ}$ C. by means of a Westphal balance, pycnometer or other convenient apparatus.

Hypochlorite and Available Chlorine.—Transfer a 20 cc. aliquot of the sample to a liter volumetric flask and dilute to volume. Pipet a 50 cc. aliquot of the diluted solution into a 200 cc. Erlenmeyer flask, and titrate with 0.1 *N* sodium arsenite solution, using starch iodide paper as an outside indicator. From the number of cubic centimeters of sodium arsenite solution used and the specific gravity of the hypochlorite solution calculate the percentage of sodium hypochlorite in the sample on the basis that 1 cc. of 0.1 *N* sodium arsenite is equal to 0.003723 gram of sodium hypochlorite.

Calculate available chlorine from the sodium arsenite titration on the basis that 1 cc. is equal to 0.003546 gram of available chlorine.

These two constituents may also be determined by thiosulfate titration, as described under "Chlorinated Lime."

Other Forms of Chlorine.—For the determination of total chlorine, chloride chlorine and chlorate chlorine, use the methods described under chlorinated lime with modifications as to the quantity of sample to be used. In calculating the forms of chlorine other than available chlorine note that the allowance to be made for the latter is only half its percentage instead of the full percentage as in the case of chlorinated lime.

Sodium Hydroxide.—Pipet 20 cc. of the sample into a 200 cc. Erlenmeyer flask. Add 50 cc. of hydrogen peroxide solution that is neutral to phenolphthalein to destroy sodium hypochlorite. Mix well and then add sufficient neutral barium chloride solution to precipitate any carbonate present. Let stand for a few minutes and titrate with 0.2 *N* sulfuric acid, using phenolphthalein as an indicator. Calculate the percentage of sodium hydroxide on the basis that 1 cc. of 0.2 *N* sulfuric acid is equivalent to 0.008001 gram of sodium hydroxide.

Carbon Dioxide.—Determine as described under "Chlorinated Lime," using a quantity of the sample governed by the quantity of CO_2 present.

CHLORAMINE T

Chloramine T (sodium paratoluenesulphonchloramide, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NaNCl}\cdot 3\text{H}_2\text{O}$) is made by the action of strongly alkaline sodium hypochlorite on paratoluenesulphonamide, the latter being a by-product of the manufacture of saccharin.

Sampling.—Use the method for sampling powders, p. 480, as it is satisfactory for sampling this material.

Active Chlorine.—*U. S. P. Method.*¹

REAGENT

Potassium iodide solution.—Dissolve 16.5 grams of potassium iodide in water and dilute to 100 cc.

DETERMINATION

Dissolve about 0.5 gram of the sample, accurately weighed, in 50 cc. of water, add 5 cc. of the potassium iodide solution and 5 cc. of acetic acid, and allow the

¹ U. S. Pharmacopeia X, 106.

mixture to stand in a glass-stoppered bottle for 10 minutes. Titrate the liberated iodine with 0.1 *N* sodium thiosulfate, using starch solution as indicator. Each cubic centimeter of 0.1 *N* sodium thiosulfate corresponds to 0.001773 gram of active chlorine. From this titration calculate the percentage of active chlorine in the sample.

Sodium arsenite method.—Weigh 2 grams of the sample, transfer to a 200 cc. volumetric flask, dissolve in water, make to the mark, and mix thoroughly. Pipet a 50 cc. aliquot into a 200 cc. Erlenmeyer flask and titrate with standard sodium arsenite solution, using starch-iodide paper as an outside indicator as described under chlorinated lime. From this titration calculate the percentage of active chlorine in the sample on the basis that 1 cc. of 0.1 *N* sodium arsenite is equivalent to 0.001773 gram of active chlorine.

Total Chlorine.—To a solution that has been titrated for active chlorine by the sodium arsenite method add a slight excess of nitric acid, neutralize the solution with calcium carbonate, and titrate with 0.1 *N* silver nitrate solution, using potassium chromate as indicator. Run a blank determination on the reagents and make correction for any chlorine found. From the corrected titration calculate the percentage of total chlorine in the sample on the basis that 1 cc. of 0.1 *N* silver nitrate solution is equivalent to 0.003546 gram of chlorine. If the total chlorine exceeds the active chlorine, the presence of sodium chloride is indicated.

Sodium.—Weigh 0.5 gram of the sample in a platinum dish and add about 25 cc. of water and 10 cc. of dilute sulfuric acid (1 + 4). Evaporate to a sirupy consistency on a steam bath and finally to dryness on a hot plate. Ignite at the full heat of a Bunsen burner, cool, and weigh as sodium sulfate. The residue should be completely soluble in water and should show no turbidity with ammonia and ammonium carbonate. Test with a flame for sodium. If the residue meets these tests it may be considered to be pure sodium sulfate. From the weight of the residue calculate the percentage of sodium in the sample.

Melting Point Test.—Dissolve 2-5 grams of the sample in water, acidify with acetic acid, filter, extract the filtrate with chloroform, and dry the chloroform solution with calcium chloride. Add petroleum ether, collect the precipitate which forms, and dry it on a porous plate. Determine the melting point of the dried precipitate and test for chlorine. This precipitate should be free from chlorine and have a melting point of 136° C.¹ Its formula is $C_7H_7SO_2NH_2$ (1:4).

DICHLORAMINE T

Dichloramine T (paratoluenesulphondichloramide, $CH_3.C_6H_4.SO_2.NCl_2$) is made by dissolving paratoluenesulphonamide in bleaching powder solution, or by dissolving chloramine T in hypochlorous acid.

Sampling.—Use the method for sampling powders, p. 480, as it is satisfactory for sampling this material.

Active Chlorine.¹—Dissolve about 0.1 gram of the sample, accurately weighed,

¹ U. S. Pharmacopeia X, 125.

² *Ber.*, 18, 2, p. 1853 (1879).

in 20 cc. of glacial acetic acid, in a dry, glass-stoppered bottle. Add 10 cc. of potassium iodide solution (described under Chloramine T) and 50 cc. of distilled water, allow the mixture to stand for 10 minutes, and titrate the liberated iodine with 0.1 *N* sodium thiosulfate, using starch solution as indicator. Each cc. of 0.1 *N* sodium thiosulfate corresponds to 0.001773 gram of active chlorine. From this titration calculate the percentage of active chlorine in the sample.

CHAPTER X

CYANIDES AND HYDROCYANIC ACID

The most important agricultural use of hydrocyanic acid is the fumigation of citrus trees for the destruction of scale insects. Such fumigation was first suggested by D. W. Coquillett¹ who began this work in 1886 in southern California.

At first the hydrocyanic acid was generated directly under the trees by the action of sulfuric acid on sodium or potassium cyanide, but during the last decade liquid hydrocyanic acid has been made commercially and is now extensively used as such in fumigation.

In addition to the use mentioned hydrocyanic acid gas is also extensively used for the fumigation of cotton bales, nursery stock, dwellings, railroad cars, ships, etc. Tear gas is sometimes used along with it as a safety measure; for instance the National Laboratory of Health has used a mixture of cyanogen chloride and hydrocyanic acid for the fumigation of ships.²

The only other cyanide product having any important insecticidal use is calcium cyanide. Its principal use is for the fumigation of greenhouses, but it is also used to kill rodents in their burrows and dens. Its easy decomposition by the action of moisture makes it particularly well suited for these purposes. The calcium cyanide is applied as a dust, and the hydrocyanic acid gas is liberated by the moisture in the air or ground.

POTASSIUM AND SODIUM CYANIDES

Potassium and sodium cyanides are made principally by the Beilby³ and Castner⁴ processes. In the former a fused mixture of potassium carbonate and charcoal is treated with ammonia. The product is a molten cyanide of high strength. This is filtered from insoluble matter and then cast in molds, yielding cakes of pure white cyanide.

In the Castner process ammonia is passed over metallic sodium, heated to 300°-400° C. in an iron retort. The sodamide formed in this reaction is then brought into contact with charcoal previously heated to dull redness, where it is converted into a very pure sodium cyanide.

¹ Univ. of California Agr. Expt. Sta. Bull. 122.

² U. S. Public Health Rpts., 43, No. 41, 2647 (1928).

³ Proc. Roy. Phil. Soc., Glasgow, 1904.

⁴ Roscoe and Schorlemmer, *A Treatise on Chemistry*, Vol. 2, 276 (1917).

Sodium and potassium cyanides as sold commercially are usually quite pure; they ordinarily contain from 96 to 99 per cent of alkali cyanide. The most common impurities are carbonates and chlorides, and it is important that cyanide for fumigation purposes be practically free from the latter.¹ These products usually appear on the market in lump forms, the lumps being perhaps several ounces in weight. Sometimes sodium cyanide is prepared specially for the use of the fumigator in the form of lumps of uniform size closely approximating 1 ounce in weight. This form is intended to facilitate the measurement of dosage in the pot method of fumigation.

Preparation of Sample.—Break the sample into small lumps (do not grind), mix, and preserve in bottles or other tight containers.

Cyanogen²

REAGENTS

- (a) *0.1 N silver nitrate solution.*—Standardize against pure sodium chloride by titration, using chromate indicator; or gravimetrically, weighing the chloride.
- (b) *Lead carbonate.*—Fine powder.
- (c) *Sodium hydroxide solution.*—Dissolve 100 grams of sodium hydroxide in water and dilute to 1 liter.
- (d) *Potassium iodide.*—Crystals or a saturated solution.

DETERMINATION

Weigh quickly about 5 grams of sample in a weighing bottle and wash into a 500 cc. volumetric flask containing about 200 cc. of water. Add a little lead carbonate to precipitate any sulfide sulfur that may be present, dilute to the mark with water, mix thoroughly, filter through a dry filter, and then transfer a 50 cc. aliquot to a 400 cc. beaker. Add 200 cc. of water, 5 cc. of the sodium hydroxide solution and 10 drops of the potassium iodide solution (or a few crystals) and titrate to a faint opalescence with the 0.1 N silver nitrate solution. (In making this titration, it is advantageous to set the beaker on a black surface.) From the number of cubic centimeters of 0.1 N silver nitrate used calculate the percentage of cyanogen (CN) in the sample. The reaction is represented by the equation: $2\text{NaCN} + \text{AgNO}_3 = \text{NaCN} \cdot \text{AgCN} + \text{NaNO}_3$; hence 1 cc. of 0.1 N silver nitrate solution is equivalent to 0.005202 gram of cyanogen (CN), 0.009801 gram of sodium cyanide (NaCN) or 0.013022 gram of potassium cyanide (KCN).

Alkali.—Transfer a 50 cc. aliquot of the solution, prepared as directed under cyanogen, to a platinum evaporating dish. Add 5 cc. of sulfuric acid (1 + 4) and evaporate on a steam bath under a hood. Use extreme care to avoid breathing any of the evolved gas during this operation. When the contents of the dish have

¹ U. S. Dept. Agr. Bur. Entomology Bull. 90, part 3.

² J. Assoc. Official Agr. Chem., 10, 27 (1927).

reached a sirupy consistency heat carefully on a hot plate or over a low Bunsen flame until all sulfuric acid fumes have been driven off. Dissolve the residue in about 40 cc. of water, make slightly alkaline with ammonia, add a few drops of ammonium carbonate solution, and heat for a few minutes. Filter into a weighed evaporating dish, evaporate to dryness, and ignite at the full heat of the Bunsen burner. Cool and weigh as sodium or potassium sulfate. The residue should be completely soluble in water, neutral, and show no turbidity with ammonia and ammonium carbonate.

Test the residue with a flame, and if only one of the alkali metals is present, calculate the percentage of sodium or potassium oxide, as the case may be.

If the flame test shows the sample to contain both sodium and potassium, determine the potash in the mixed sulfates by the chloroplatinate method.

Chlorine.—Formaldehyde Method ¹

REAGENTS

(a) 0.1 *N* silver nitrate solution.—Prepare as directed under cyanogen in sodium and potassium cyanides, Reagent (a).

(b) 0.1 *N* ammonium or potassium thiocyanate solution.—Adjust by titrating against the 0.1 *N* silver nitrate solution, using ferric alum indicator (d).

(c) Formaldehyde solution.—A 40 per cent chloride-free solution.

(d) Ferric alum indicator.—A saturated solution of ferric ammonium alum.

DETERMINATION

Transfer a 50 cc aliquot of the solution prepared for the determination of cyanogen to a beaker, dilute with an equal volume of water, add 1-2 cc. of the formaldehyde solution, stir well, and let stand for 15 minutes. Acidify with nitric acid (5 cc. of 1 + 1 is usually enough), add a measured volume of the 0.1 *N* silver nitrate solution sufficient to give an excess, stir well, filter, wash, and titrate the excess silver in the combined filtrate and washings with the 0.1 *N* thiocyanate solution, using ferric indicator. From the number of cubic centimeters of 0.1 *N* silver nitrate solution, less the number of cubic centimeters of 0.1 *N* thiocyanate solution used, calculate the percentage of chlorine in the sample, on the basis that each cubic centimeter of 0.1 *N* silver nitrate is equivalent to 0.003546 gram of chlorine.

Distillation Method¹

REAGENTS

The reagents needed are described under the formaldehyde method.

DETERMINATION

Transfer a 50 cc. aliquot of the solution prepared for the determination of cyanogen to a distilling flask, dilute to 100-150 cc., acidify with a slight excess of acetic acid, and distil, passing the vapors through a condenser, the delivery end of which dips into a solution of sodium hydroxide, to absorb the hydrocyanic acid and

¹ *J. Assoc. Official Agr. Chem.*, 10, 28 (1927).

thus protect the analyst from the fumes. After all the hydrocyanic acid has been driven off, which should be the case when 50 cc. of distillate has passed over, wash the liquid remaining in the distilling flask into a beaker, add 5 cc. of dilute nitric acid ($1 + 1$) and then a measured volume of the $0.1\ N$ silver nitrate solution sufficient to give an excess, stir well, filter, wash, and titrate the excess of silver in the combined filtrate and washings with the $0.1\ N$ thiocyanate solution, using ferric indicator. From the number of cubic centimeters of $0.1\ N$ silver nitrate solution, less the number of cubic centimeters of $0.1\ N$ thiocyanate solution used, calculate the percentage of chlorine in the sample.

Carbon Dioxide.—*Evolution Method*

APPARATUS

The apparatus consists of a 200 cc. Erlenmeyer flask closed with a 2-holed stopper; one hole is fitted with a dropping funnel, the stem of which extends almost to the bottom of the flask, and the outlet of a condenser passes downward through the other hole. The upper end of the condenser is connected with a calcium chloride tube (many samples of calcium chloride contain free lime and it is necessary to select a neutral preparation for use in this tube), which in turn is connected with a Geissler bulb containing concentrated sulfuric acid. Next in line are two weighed U-tubes for absorbing the carbon dioxide, the first filled with porous soda-lime and the second, one-third with soda-lime and two-thirds with calcium chloride, the calcium chloride being placed at the exit end of the train. An aspirator is connected to the last U-tube to draw air through the apparatus. An absorption tower filled with soda-lime is connected with the mouth of the dropping funnel to remove carbon dioxide from the air entering the apparatus.

DETERMINATION

Weigh 1 gram of the sample into the Erlenmeyer flask, add about 20 cc. of water, and allow the sample to dissolve; then add 4 grams of silver nitrate dissolved in about 50 cc. of water. Mix by rotating the flask and connect the flask to the apparatus, omitting the two weighed U-tubes and draw carbon dioxide-free air through the apparatus until the original air is displaced. Then attach the weighed U-tubes in position as described above, close the stopcock of the dropping funnel, pour into it 50 cc. of dilute nitric acid ($1 + 1$), reconnect with the soda-lime tower, and allow the acid to flow into the Erlenmeyer flask. When effervescence diminishes, place a low Bunsen flame under the flask and start the flow of water through the condenser, drawing a slow current of air through the apparatus at the same time. Maintain a steady but quiet ebullition and a slow air current through the apparatus. Boil for a few minutes after the water has begun to condense, then remove the flame and continue the aspiration of air at the rate of about two bubbles per second until the apparatus is cool. Disconnect the weighed absorption tubes, cool in the balance case, and weigh. The increase in weight is the quantity of carbon dioxide liberated from the sample. From this weight calculate the percentage of carbon dioxide in the sample.

Precipitation Method

The following method is essentially that given by W. H. Seamon.¹

Weigh 10 grams of the sample in a 200 cc. beaker, dissolve in about 100 cc. of water, filter, and wash thoroughly. Catch the filtrate in a beaker and add sufficient calcium nitrate to precipitate the carbonate. Stir thoroughly and allow to stand 1 hour. Filter, wash the precipitate, ignite to constant weight over a blast lamp, and weigh as calcium oxide. From this weight calculate the percentage of carbon dioxide in the sample, using the factor, $\text{CO}_2/\text{CaO} = 0.7847$.

If preferred, transfer the washed precipitate to the flask of the apparatus described under the evolution method and determine the carbon dioxide by evolution. In this case omit the silver nitrate in the evolution flask and use dilute hydrochloric acid for the liberation of the carbon dioxide. With these exceptions proceed as directed in the evolution method.

Moisture.—Dry 2 grams of sample to constant weight at 105° C. and calculate the percentage loss in weight as moisture.

The carbon dioxide and moisture content of cyanides is relatively unimportant and these determinations may generally be omitted. The determinations usually made in testing sodium or potassium cyanide are cyanogen, chlorine and alkali.

CALCIUM CYANIDE

Impure calcium cyanide is made by fusing calcium cyanamide, calcium carbide and sodium chloride in an electric furnace. The fused mass is ground and is marketed as flake, granular or dust calcium cyanide.

The product contains from 40 to 45 per cent of calcium cyanide. The principal impurities are calcium carbonate and sodium chloride, with smaller quantities of sulfides, carbon, calcium carbide, calcium cyanamide and siliceous material.

Another method of manufacture used to some extent for several years consisted of treating calcium carbide with liquid hydrocyanic acid. The product obtained contained a higher percentage of cyanogen than that obtained by fusion in the electric furnace, and it consisted of calcium cyanide in combination with hydrocyanic acid ($\text{Ca}(\text{CN})_2 \cdot 2\text{HCN}$).

Cyanogen.²

REAGENTS

(a) 0.1 *N* silver nitrate solution.—Prepare as directed under cyanogen in sodium and potassium cyanides, Reagent (a), p. 543.

(b) Soda-lead reagent.—Dissolve 20 grams of lead acetate in water, dilute to 1 liter, and add 200 grams of chloride-free sodium carbonate.

¹ *Western Chem. Met.*, **5**, 292 (1909).

² *J. Assoc. Official Agr. Chem.*, **10**, 29 (1927).

(c) *Sodium hydroxide solution*.—Prepare as directed under sodium and potassium cyanides, Reagent (c).

(d) *Potassium iodide*.—Crystals or a saturated solution.

DETERMINATION

Place about 200 cc. of water in a 500 cc. volumetric flask and carefully dry the neck of the flask. Weigh about 5 grams of the sample in a weighing bottle and transfer to the flask with the least possible exposure to the air. Wash down into the flask and mix by whirling until the soluble portion is completely dissolved and the small quantity of calcium carbide has been decomposed. Then add 25 cc. of the well-mixed soda-lead reagent, or a quantity sufficient to remove sulfides, close the flask with a rubber stopper, and shake thoroughly at intervals over a period of 30 minutes. Dilute to the mark, mix, and filter through a dry filter. Transfer a 50 cc. aliquot to a 400 cc. beaker and proceed as directed under the determination of cyanogen in sodium and potassium cyanides, beginning with "Add 200 cc. of water, 5 cc. of sodium hydroxide solution, ****." One cc. of 0.1*N* silver nitrate solution is equivalent to 0.005202 gram of cyanogen (CN). To obtain the percentage of calcium cyanide ($\text{Ca}(\text{CN})_2$), multiply the percentage of cyanogen by the factor 1.7702.

Chlorine.—Determine chlorine by the formaldehyde or the distillation method, as described under sodium and potassium cyanides, using a 50 cc. aliquot of the solution prepared for the determination of cyanogen.

Water-Insoluble Residue.—Weigh 2 grams of the sample into a beaker, add 100 cc. of water, and stir. Allow to stand for 30 minutes, stirring at frequent intervals. Filter through a weighed Gooch crucible and wash with water at room temperature. Dry the residue at 105° C. and weigh. From this weight calculate the percentage of water-insoluble residue. This residue will consist chiefly of calcium carbonate with small quantities of carbon and silica.

HYDROCYANIC ACID (LIQUID)

Liquid hydrocyanic acid has been known for many years, but only during the last decade has it been manufactured on a large scale. At the present time this material has almost entirely replaced the alkali cyanides in the fumigation of citrus trees for scale insects. Large quantities are also used in the fumigation of bale cotton and other imported materials, as well as the cars and ships bringing them, to prevent the introduction of insect pests. In the fumigation of cotton and freight cars entering the United States from Mexico alone, the Federal Horticultural Board used over 100,000 pounds of hydrocyanic acid during the years 1927 and 1928.

Liquid hydrocyanic acid is colorless, has a specific gravity of 0.697 at 18° C. and a boiling point of 26.5° C., and is miscible with water in all

proportions. It is ordinarily stable, but it has been known to suffer decomposition, with explosive violence. The product manufactured at present has been much improved in its keeping qualities, and the explosive hazard is now of minor importance.

Gray and Hulbirt¹ recognized the difficulty of sampling and analyzing such a poisonous and volatile material and proposed a specific gravity method for obtaining its strength. They prepared tables for this purpose and obtained results which agreed very well with those obtained by a careful chemical analysis.

Walker and Marvin² prepared, for use with hydrometers accurately graduated at 15.6° C., a table of percentages corresponding to specific gravity, which they claim to be more accurate than the table of Gray and Hulbirt. They state that long and continuous use of this table has demonstrated that the results of the determination of hydrocyanic acid by the specific gravity method are accurate to within ± 0.1 per cent.

Hydrocyanic Acid.—*Specific Gravity Method*

APPARATUS

The apparatus, shown in Fig. 4, consists of a hydrometer enclosed in a glass tube which is closed at each end with a 2-hole rubber stopper. A piece of tubing containing a stopcock passes through each of the holes in the lower stopper. One of these tubes passes through another 2-hole stopper and is used to draw the sample from the drum or bottle. A thermometer projects into the liquid through the upper stopper and a suction bulb is also attached to the upper stopper for pumping the liquid from the container into the tube.

The hydrometer is graduated at 15.6° C. and is accurate to the third decimal place.

DETERMINATION

Place the apparatus in position with the tube inserted in the drum or bottle containing the sample, pump up sufficient liquid to float the hydrometer, note the temperature, and read the specific gravity to 3 decimal places. Use these data to obtain the percentage of hydrocyanic acid from Table I.

¹ Univ. California Agr. Expt. Sta. Bull. 308.

² *Ind. Eng. Chem.*, 18, 139 (1926).

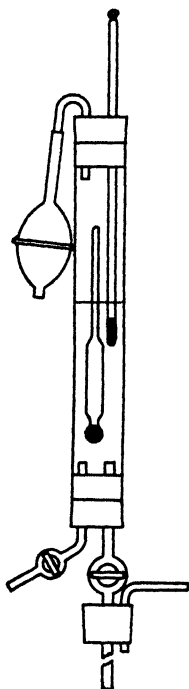


FIG. 4.—Apparatus for Determination of Hydrocyanic Acid by Specific Gravity.

*Titration Method*¹

APPARATUS

In this method weighing the charge for analysis and getting it absorbed in alkali are the only difficulties encountered. The following apparatus (Fig. 5) is desirable: The sampling tube, *A*, is fitted with two 3-way stopcocks, one of which communicates with the air and is protected by a soda-lime guard tube, *C*, while the other communicates directly with the 500 cc. sample bottle, *D*, and also with the 200 cc. absorption flask, *B*. The connection with Flask *B* is made by means of an intermediate bulb, *E*, carrying a short stem on the upper end and a long slender stem on the lower end. The absorption flask is protected by a soda-lime guard tube, *F*, against any moisture which may diffuse backward from a filter pump to which it is attached. The glass cylinder, *G*, under one outlet from the upper stopcock catches the overflow.

ABSORPTION OF HYDROCYANIC ACID

Place 90 cc. of 25 per cent sodium hydroxide solution in the absorption flask. Insert the stopper carrying the bulb and carefully weigh the flask and contents.

¹ *Ind. Eng. Chem.*, 18, 139 (1926).

TABLE I.—FOR DETERMINATION OF PERCENTAGE OF HYDROCYANIC ACID FROM SPECIFIC GRAVITY AND TEMPERATURE.
FOR USE WITH HYDROMETERS GRADUATED AT 15.6° C.

[illegible]

0.714	90.9	90.5	90.1	98.6	98.2	97.8	97.3	96.9	96.5	96.0	95.6	95.2	94.8	94.4	94.0	93.5	93.2	92.7	92.3	91.9	91.6	91.2	90.8
0.715	100.0	90.6	99.2	98.8	98.3	97.9	97.5	97.0	96.6	96.2	95.7	95.3	94.9	94.5	94.1	93.7	93.3	92.9	92.5	92.1	91.7	91.3	90.9	90.5
0.716	99.7	99.3	98.9	98.4	98.0	97.6	97.1	96.7	96.3	95.9	95.4	95.0	94.6	94.2	93.8	93.4	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.3
0.717	99.8	99.4	99.0	98.6	98.1	97.7	97.3	96.8	96.4	96.0	95.6	95.1	94.7	94.3	93.9	93.5	93.1	92.7	92.3	91.9	91.5	91.1	90.7	90.3	90.0
0.718	100.0	99.5	99.1	98.7	98.2	97.8	97.4	97.0	96.5	96.1	95.7	95.3	94.8	94.4	94.0	93.6	93.2	92.8	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.7	89.4
0.719	99.6	99.2	98.8	98.4	97.9	97.5	97.1	96.7	96.2	95.8	95.4	95.0	94.5	94.1	93.7	93.3	92.9	92.5	92.1	91.7	91.3	90.9	90.5	90.1	89.8	89.4	
0.720	99.3	98.9	98.5	98.1	97.6	97.2	96.8	96.4	95.9	95.5	95.1	94.7	94.2	93.8	93.4	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.2	89.8	89.5	89.1	
0.721	99.0	98.6	98.2	97.7	97.3	96.9	96.5	96.0	95.6	95.2	94.8	94.3	93.9	93.5	93.1	92.7	92.3	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.2	88.8	
0.722	98.7	98.3	97.9	97.4	97.0	96.6	96.2	95.7	95.3	94.9	94.5	94.0	93.6	93.2	92.8	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.9	88.5	
0.723	98.4	98.0	97.5	97.1	96.7	96.3	95.9	95.4	95.0	94.6	94.2	93.7	93.3	92.9	92.5	92.1	91.7	91.3	90.9	90.5	90.1	89.7	89.3	89.0	88.6	88.2	
0.724	98.1	97.7	97.2	96.8	96.4	96.0	95.6	95.1	94.7	94.3	93.9	93.4	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.2	89.8	89.4	89.0	88.7	88.3	87.9	
0.725	97.8	97.3	96.9	96.5	96.1	95.7	95.2	94.8	94.4	94.0	93.6	93.1	92.7	92.3	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.4	88.0	87.7	
0.726	97.4	97.0	96.6	96.2	95.8	95.4	94.9	94.5	94.1	93.7	93.2	92.8	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.1	87.7	87.4	
0.727	97.1	96.7	96.3	95.9	95.5	95.1	94.6	94.2	93.8	93.4	92.9	92.5	92.1	91.7	91.3	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.2	87.8	87.4	87.1	
0.728	96.8	96.4	96.0	95.6	95.2	94.8	94.3	93.9	93.5	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.5	87.1	86.8	
0.729	96.5	96.1	95.7	95.3	94.9	94.5	94.0	93.6	93.2	92.7	92.3	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.6	87.2	86.8	86.5	
0.730	96.2	95.8	95.4	95.0	94.6	94.2	93.7	93.3	92.9	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.3	86.9	86.6	86.2	
0.731	95.9	95.5	95.1	94.7	94.2	93.8	93.4	93.0	92.6	92.1	91.7	91.3	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.7	87.3	87.0	86.6	86.3	85.9	
0.732	95.6	95.2	94.8	94.3	93.9	93.5	93.1	92.7	92.3	91.8	91.4	91.0	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.4	87.1	86.7	86.3	86.0	85.6	
0.733	95.3	94.9	94.5	94.0	93.6	93.2	92.8	92.4	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.5	87.1	86.8	86.4	86.1	85.7	85.3	
0.734	95.0	94.6	94.1	93.7	93.3	92.9	92.5	92.1	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.2	86.8	86.5	86.1	85.8	85.4	85.1	
0.735	94.6	94.2	93.8	93.4	93.0	92.6	92.2	91.8	91.3	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.7	87.3	86.9	86.6	86.2	85.8	85.5	85.1	84.8	
0.736	94.3	93.9	93.5	93.1	92.7	92.3	91.9	91.5	91.0	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.4	87.0	86.6	86.3	85.9	85.5	85.2	84.8	84.5	
0.737	94.0	93.6	93.2	92.8	92.4	92.0	91.6	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.5	87.1	86.7	86.3	86.0	85.6	85.2	84.9	84.5	84.2	
0.738	93.7	93.3	92.9	92.5	92.1	91.7	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.2	86.8	86.4	86.0	85.7	85.3	84.9	84.6	84.2	83.9	
0.739	93.4	93.0	92.6	92.2	91.8	91.4	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.7	87.3	86.9	86.5	86.1	85.7	85.4	85.0	84.6	84.3	84.0	83.6	
0.740	93.1	92.7	92.3	91.9	91.5	91.1	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.4	87.0	86.6	86.2	85.8	85.4	85.1	84.7	84.3	84.0	83.7	83.3	
0.741	92.8	92.4	92.0	91.6	91.2	90.8	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.4	87.1	86.7	86.3	85.9	85.5	85.1	84.8	84.4	84.1	83.7	83.4	83.1	
0.742	92.4	92.1	91.7	91.3	90.9	90.5	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.1	86.8	86.4	86.0	85.6	85.2	84.8	84.5	84.1	83.8	83.4	83.1	82.8	
0.743	92.1	91.8	91.3	90.9	90.5	90.2	89.7	89.3	88.9	88.5	88.1	87.6	87.3	86.8	86.5	86.1	85.7	85.3	84.9	84.5	84.2	83.8	83.5	83.1	82.8	82.5	
0.744	91.8	91.4	91.0	90.6	90.2	89.9	89.4	89.0	88.6	88.2	87.8	87.3	87.0	86.5	86.2	85.8	85.4	85.0	84.6	84.2	83.9	83.5	83.2	82.8	82.5	82.2	
0.745	91.5	91.1	90.7	90.3	89.8	89.6	89.1	88.7	88.3	87.9	87.4	87.0	86.7	86.2	85.9	85.5	85.1	84.7	84.3	84.0	83.6	83.2	82.9	82.5	82.2	81.9	
0.746	91.2	90.8	90.4	90.0	89.6	89.3	88.8	88.4	88.0	87.6	87.1	86.7	86.3	85.9	85.6	85.2	84.8	84.4	84.0	83.7	83.3	82.9	82.6	82.3	81.9	81.6	
0.747	90.9	90.5	90.1	89.7	89.3	89.0	88.5	88.1	87.7	87.3	86.8	86.4	86.0	85.6	85.3	84.9	84.5	84.1	83.7	83.4	83.0	82.6	82.3	82.0	81.6	81.3	
0.748	90.6	90.2	89.8	89.4	89.0	88.7	88.2	87.8	87.3	86.9	86.5	86.1	85.7	85.3	84.9	84.6	84.2	83.8	83.4	83.1	82.7	82.3	82.0	81.7	81.4	81.0	
0.749	90.3	89.9	89.5	89.1	88.7	88.4	87.9	87.5	87.0	86.6	86.2	85.8	85.4	85.0	84.6	84.3	83.9	83.5	83.1	82.8	82.4	82.0	81.7	81.4	81.1	80.7	
0.750	90.0	89.6	89.2	88.8	88.4	88.1	87.6	87.2	86.7	86.3	85.9	85.5	85.1	84.7	84.3	84.0	83.6	83.2	82.8	82.5	82.1	81.7	81.4	81.1	80.8	80.4	

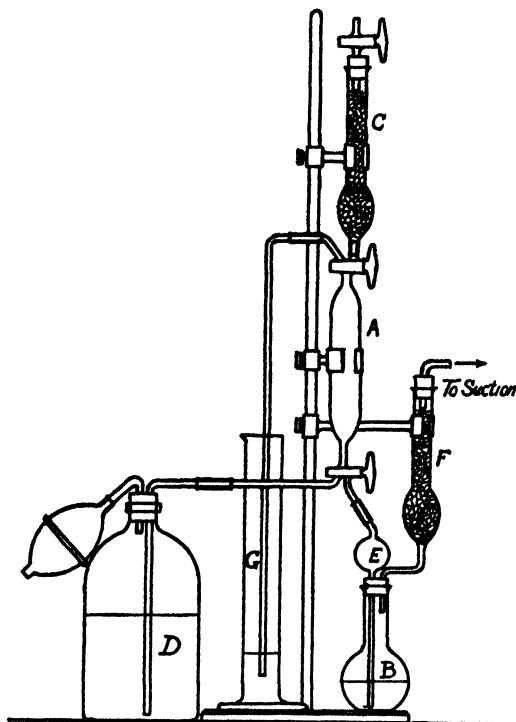


FIG. 5.—Apparatus for Determination of Hydrocyanic Acid by Titration Method.

Attach the flask to the absorption apparatus and turn the stopcock so that the hydrocyanic acid may flow from the sample bottle through the receiving bulb and out into the cylinder. Connect the 500 cc. bottle containing the sample to be analyzed, and pump the liquid hydrocyanic acid through the apparatus until both are at the same temperature and no loss by volatilization due to the heat of the apparatus may occur. Next close the lower stopcock and then close the upper one. Then cautiously open the lower stopcock so that only a very small stream flows down through the empty bulb on the absorbing flask, in which space the liquid is vaporized and then bubbles slowly under perfect control through the soda-solution, where it is completely absorbed. Owing to the relatively high vapor pressure of the hydrocyanic acid the liquid will be forced out of the sampling bulb without opening the upper stopcock. After the sampling bulb has thus been gradually emptied of the liquid, apply gentle suction to the lower guard tube, open the upper stopcock by turning to connect with the soda-lime tube which is opened to the air, and slowly draw a current of air through the liquid in the absorption flask, thus removing all traces of hydrocyanic acid from the receiving bulb. Detach the absorber, remove the guard tube, and after cooling in the balance case, reweigh the flask and contents. The increase in weight is due to the absorbed hydrocyanic acid. Transfer the contents

of the absorber to a liter flask, make to volume, mix well, and determine the hydrocyanic acid in an aliquot by titration as described under sodium cyanide.

HYDROCYANIC ACID IN FUMIGATED PRODUCTS

As a result of the fumigation of warehouses and other storage places foodstuffs often absorb and retain more or less of the hydrocyanic acid. The question of the quantity retained has been investigated by Griffin, Neifert, Perrine, Duckett and Back.¹ They found that all the products examined absorbed the fumigant to some extent, but the proportion absorbed varied with the different products, as did the rate at which the hydrocyanic acid was evolved during subsequent storage. The method of determination follows:

REAGENTS

- (a) *Normal sodium hydroxide*.—Prepare an approximately normal solution by dissolving 40 grams of sodium hydroxide in 1 liter of water.
- (b) *Ferrous sulfate solution*.—Dissolve 3 grams of ferrous sulfate in 100 cc. of water. This reagent should be freshly prepared.
- (c) *Powdered potassium fluoride*.
- (d) *Crystallized tartaric acid*.

DETERMINATION

Weigh a quantity of the sample containing the equivalent of 1–2 mg. of potassium cyanide, transfer to a 500 cc. distilling flask, and add about 200 cc. of water and 5–10 grams of tartaric acid. Attach to a condenser and distil about 50 cc. into a 250 cc. round-bottom flask containing 1 cc. of the normal sodium hydroxide. During the distillation use an adapter attached to the condenser so that it dips under the surface of the liquid in the receiving flask. Determine the hydrocyanic acid in the distillate by the method of Viehoveer and Johns,² as follows:

Concentrate the distillate to a volume of 1 cc. by distillation under reduced pressure, using a filter pump. In order to induce smooth and regular evolution of the water vapor, admit air into the flask through a capillary tube dipping into the liquid. Apply heat for the distillation by immersing the flask in a beaker of water, which is kept at a temperature of 65° C.

When the liquid has been concentrated to 1 cc., add from 0.2 to 0.5 cc. of the freshly prepared ferrous sulfate solution and about 0.05 gram of potassium fluoride. Exhaust the flask again by means of the water vacuum pump, and mix the contents by rotating the flask. After 5–10 minutes detach the flask from the pump and acidify the mixture with 30 per cent nitric acid. The blue color will at once appear. If only traces of hydrocyanic acid are present, it will sometimes be necessary to warm to about 50° C. in a water bath to develop the color. After the color has developed,

¹ U. S. Dept. Agr. Bull. 1149 and 1307.

² Am. Chem. Soc., 37, 601 (1915).

dilute to a volume that will give a color intensity convenient to compare with a set of standard suspensions of Prussian blue made from known weights of potassium cyanide. Standards equivalent to 0.2–1.5 mg. of potassium cyanide diluted to 25 cc. will give colors of convenient intensity. Keep the mixtures protected from the air and avoid much shaking, to prevent excessive oxidation of the ferrous hydroxide.

The quantities of reagents mentioned are suitable for 1–2 mg. of potassium cyanide. If less than 1 mg. of potassium cyanide is present, reduce the quantities of the reagents accordingly, in order to obtain the maximum intensity of color. From the results obtained by comparison with the standards, calculate the quantity of hydrocyanic acid in the sample and report as parts per million.

CHAPTER XI

MERCURY COMPOUNDS

The disinfectant or germicidal action of the compounds of mercury is too well known to need much comment. The chloride is widely used as a disinfectant and, like the iodide, is added to soaps to make them antiseptic; the metal itself is incorporated into ointments for use against certain fungous infections of the skin, for certain insects on man, and lice on chickens. Recently various organic compounds containing mercury have attained considerable reputation as seed disinfectants, finding use, for instance, in preventing the spread of stinking smut in wheat. Finally, mercuric chloride finds limited application as an insecticide, being used in aqueous solution or in kerosene, gasoline or other volatile liquid for control of bed bugs.

The analysis of mercury preparations presents many points of interest and frequently considerable difficulty. In the first place many mercuric salts are only slightly ionized, which makes it difficult to precipitate the acid radicle; for instance, silver salts will not precipitate the cyanide radicle from a solution of mercuric cyanide. On the other hand this property forms the basis of methods for estimating the mercury; for instance, a solution of mercuric nitrate may be titrated with a solution of a thiocyanate, the mercury becoming mercuric thiocyanate, which although soluble is so little ionized that it does not color the ferric salt solution used as an indicator for excess thiocyanate. Practically all inorganic mercury compounds, however, yield a quantitative precipitate with hydrogen sulfide, due to the extreme insolubility of mercuric sulfide.

Some organic compounds of mercury resist even the action of hydrogen sulfide, and it is necessary to resort to other means of separating the element. Electrolysis will suffice in many instances, but in general it becomes necessary to destroy the organic portion of the sample and then recover the mercury by any convenient method. The destruction of organic matter has been studied by many investigators nearly all of whom have used methods involving heating with concentrated sulfuric acid to which some powerful oxidizer is added. Nitric acid is most commonly used, but permanganate and 30 per cent hydrogen peroxide have also been used. It is generally conceded that it is necessary to use a reflux condenser in such digestions in order to prevent loss of mercury by volatilization. The chance of loss is greater in the presence of chlor-products—for instance in the case of some seed disinfectants that contain mercuric chlorphenol.

PRODUCTS CONTAINING METALLIC MERCURY

Ointments containing metallic mercury are sometimes used for the control of lice on chickens. Such ointments usually consist of lard or other fatty material in which the metallic mercury has been incorporated by triturating. Numerous methods have been suggested for the analysis of these mercurial ointments. Most of these are outlined below, and in addition details are given for one method which is considered sufficiently satisfactory to use on those preparations sold as insecticides.

Jaenicke¹ simply extracts the base of the ointment with petroleum ether, evaporates the ether, and weighs the base, obtaining the percentage of mercury by difference. Johnson² treats the ointment with warm benzene and adds potassium cyanide and a few copper beads. The mercury amalgamates with the copper, the beads are recovered and weighed, and the mercury is determined by loss in weight on ignition. Weinland and Ensgraber³ dissolve the ointment in ether and benzene, dissolve the mercury by adding chlorine water, then precipitate and weigh it as mercuric sulfide. Willen⁴ extracts with ether, adds excess of standard iodine solution to dissolve the mercury, and titrates back with a standard thiosulfate solution. Crewe⁵ saponifies the fatty constituents, rendering them soluble in water, then filters off the mercury and weighs it.

Following is the simple scheme employed in the writers' laboratory.

Mercury.—Warm 5-10 grams of the sample, add 50 cc. of petroleum ether, allow the metallic mercury to settle, and decant the ether layer through a small filter. Repeat the treatment with ether until all fatty material has been dissolved.

Pour 30 cc. of concentrated nitric acid through the filter which has been used, and catch it in the beaker containing the bulk of the mercury. Let stand until the mercury has completely dissolved, make up to 250 cc. in a volumetric flask, mix, and use a 25-50 cc. aliquot for titration as follows. Add 5 cc. of 10 per cent ferric sulfate solution as indicator, and run in standard potassium thiocyanate solution (about 0.1 *N*) until a reddish yellow color is produced. Calculate the percentage of mercury on the basis that each cubic centimeter of 0.1 *N* thiocyanate solution is equal to 0.01003 gram of mercury (Hg).

Fatty Material.—Evaporate the ether extract from the mercury determination in a tared beaker and weigh the total fat.

If it is desired to investigate the fatty material more closely, proceed as follows:

Unsaponifiable Matter.—Melt the fats obtained under determination of total

¹ *Pharm. Ztg.*, **59**, 363 (1914).

² *Pacific Pharm.*, **3**, 38 (1909).

³ *Süddeut. Apoth. Ztg.*, **52**, 422 (1912).

⁴ *Schweiz. Wochschr.*, **43**, 250 (1910).

⁵ *Pharm. J.*, **81**, 359 (1908).

base, transfer to an Erlenmeyer flask fitted with a reflux air condenser, add 2 grams of potassium hydroxide and 60 cc. of 70 per cent ethyl alcohol, and heat on a steam bath for $\frac{1}{2}$ -2 hours. Evaporate the alcohol, and extract the unsaponifiable matter with several portions of ether. Evaporate the ether in a tared beaker, weigh the residue, and calculate it to percentage of unsaponifiable matter.

Fatty Acids.—Acidify the aqueous liquid left from the above determination with dilute sulfuric acid, extract with several portions of ether, evaporate the ether in a tared beaker, weigh, and calculate the residue to percentage of fatty acids.

SOAPS CONTAINING MERCURY

Mercuric chloride or mercuric iodide is sometimes added to soap to give it disinfectant properties. These mercury compounds sometimes enter into combination with the fatty acids in such a way that simple acidification of an aqueous solution of the product with hydrochloric acid does not suffice to separate the fatty acids and the mercury. However, digestion with aqua regia will usually accomplish this purpose and such preparations may be analyzed for mercury as follows:

Mercury.—Add 25 cc. of aqua regia to 5 grams of soap in a covered beaker. Digest on the steam bath for 1 hour, dilute with water, add several grams of paraffin to collect the fats and fatty acids, allow the whole to cool, remove the solid cake of fat, and determine the mercury in the aqueous layer as follows:

Nearly neutralize the acid solution with sodium carbonate and add a slight excess of freshly prepared ammonium sulfide. Add sodium hydroxide solution until the black liquid begins to clear up, then boil and add more alkali until it is completely clear. Next add an excess of ammonium nitrate and boil until the free ammonia is almost entirely expelled. Filter through a Gooch crucible and wash with hot water until all soluble sulfides are removed. Dry at 110° C. and weigh. Calculate the weight of mercuric sulfide to percentage of mercury or whatever compound qualitative tests have shown to be present.

ORGANIC MERCURIAL SEED DISINFECTANTS

As previously mentioned under copper carbonate, the disinfection of seed, especially wheat, to prevent the spread of fungous diseases, has assumed considerable importance in recent years. It is only natural that compounds of mercury should have been tried for this purpose, and they have proved especially valuable. Mercuric chloride has been used, but the greatest benefit has been derived from organic compounds of mercury. These include such products as mercury chlor-phenol, mercury nitro-phenol, resorcin mercury, sodium cresol mercury, and numerous others.

At present, no particular compound of this type is considered more active than another, and for analytical purposes it is sufficient to consider

only the mercury content. If at the same time the analyst can identify the compound present, so much the better. Such identification can usually be made by qualitative tests, and the percentage of compound present can then be calculated from the mercury content.

The determination of mercury in this class of compounds requires special pretreatment to render the mercury precipitable or titratable by the ordinary reagents. The pretreatment consists ordinarily of the digestion of the material with concentrated sulfuric acid and some powerful oxidizer, such as nitric acid, potassium permanganate, potassium dichromate, or hydrogen peroxide. In all such oxidations care must be taken to prevent the escape of mercury by volatilization, especially when the product contains chlorine compounds. This volatilization can be prevented by the use of an air condenser on the digestion flask.

An excellent review of the question of destroying organic matter preparatory to the determination of mercury has been given by Bodnar, Roth and Tergina,¹ and the following method first proposed by Wöber has been taken from their publication.

Mercury.—*Titration Method.*—Place a 0.2-0.5 gram sample in a 200 cc. Erlenmeyer flask, add 5 cc. of concentrated sulfuric acid, and mix by rotating the flask. Put a reflux condenser on the flask, warm it to 50°-60° C., and add 1-2 cc. of perhydrol dropwise through the condenser tube. After the first violent reaction is over the contents of the flask are reheated, until the carbonaceous material is completely oxidized and the solution is colorless (in the absence of course of colored salts, as those of copper).

If it is known that the sample contains no chlorides, transfer the solution resulting from the digestion just described to a beaker, and destroy the excess of hydrogen peroxide by the careful addition of a strong solution of potassium permanganate. Then remove the slight excess of permanganate by the addition of a few cubic centimeters of a ferrous ammonium sulfate solution, add 10 cc. of concentrated nitric acid, and titrate with an approximately 0.04 *N* solution of ammonium thiocyanate. Calculate the percentage of mercury on the basis that 1 cc. of 0.04 *N* thiocyanate solution is equivalent to 0.004012 gram of mercury.

If the sample is known to contain chlorides, the simple process outlined above will not suffice, since the chloride ion binds some of the mercury so tightly that it cannot be titrated. In this case the mercury should be separated from the chloride. The following method is recommended.

Transfer the acid solution resulting from the digestion with sulfuric acid and hydrogen peroxide to a 200 cc. Erlenmeyer flask, dilute it to 20-25 cc., and add concentrated sodium hydroxide solution to alkaline reaction, keeping the solution cool all the time. (Mercury will not separate at this point.) Add 15 cc. of 10 per cent formaldehyde solution, mix well, and allow to stand 30 minutes at room temperature (not below

¹ *Z. anal. Chem.*, **74**, 81 (1928).

20° C.). Filter on a 589 blue ribbon paper, or on a glass-filter (the ones marked < 7 are suitable) under suction. Wash with water until all chlorides have been removed. Dissolve the mercury in 10 cc. of concentrated nitric acid, transfer it to the flask in which the reduction took place, and titrate with standard thiocyanate solution in the manner described above.

It is also stated by the same authors that copper, arsenic, and iron do not interfere with this method of determining mercury. This is quite fortunate, since at times both copper compounds and arsenic compounds are mixed with organic

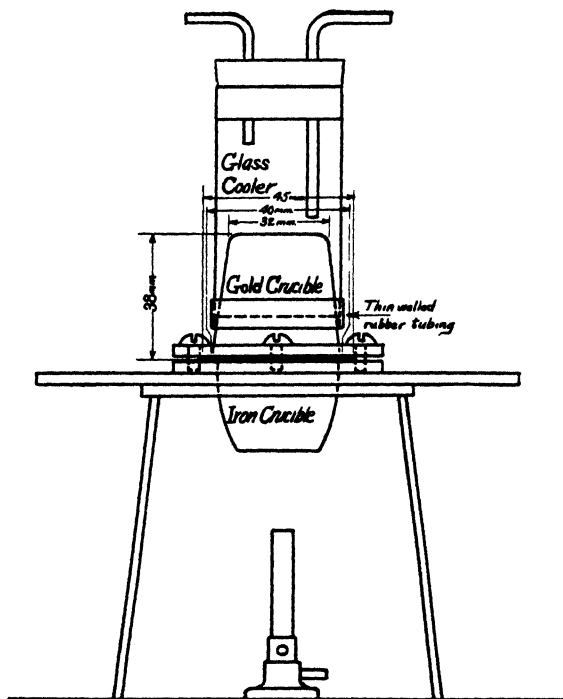


FIG 6.—Apparatus for Determination of Mercury by Volatilization.

mercury seed disinfectants. The copper may cause a little trouble because of its color, but suitable dilution will usually overcome that difficulty.

Volatilization Method.—Practically all mercury compounds are decomposed by heating with lime or other basic materials, the mercury being volatilized. This property has been made the basis for numerous methods of estimating mercury in which the volatilized mercury is either condensed in cooled tubes or caught on gold foil, or wire, with which it readily amalgamates. F. C. Whitmore¹ describes one such method which appears particularly adaptable to the analysis of seed disinfectants

¹ Organic Compounds of Mercury, Amer. Chem. Soc. Monograph Ser. Chemical Catalog Co., 1921, p. 365.

APPARATUS

The apparatus, Fig. 6, consists of two flanged crucibles which can be clamped mouth to mouth by means of two rings and holding screws. The lower crucible is made of iron, the upper of gold, and the opening of the gold one is slightly larger than that of the other so that there will be no tendency for the mercury to lodge in the joint between the two flanges. The gold crucible is cooled by circulating water through a large tube attached to it by Gooch tubing.

DETERMINATION

Weigh 1 gram of sample into the iron crucible and mix it intimately with 5 grams of anhydrous sodium carbonate. Cover the mixture with a thin layer of sodium carbonate and then with 10 grams of finely powdered barium carbonate. Place the weighed gold crucible in place, clamp the two together, set the iron crucible in a hole in a piece of asbestos board, start the cooling water, and gently heat the iron crucible. Heat below red heat for 30 minutes, cool, remove the gold crucible, wash it with 95 per cent alcohol, dry with the heat of the hand, and then place in a calcium chloride desiccator until it attains constant weight. The increased weight represents the mercury in the sample. If the sample contains more than 12 per cent mercury, less than 1 gram should be used since 0.12 gram of mercury is about all that the gold crucible can safely retain. The mercury can be removed from the gold crucible preparatory to another experiment by a short ignition at a dull red heat. This ignition should be made under a hood with a good draft.

The residue from the determination may after solution in nitric acid be used for the determination of chlorine or other halogen, provided the reagents used are halogen free.

CHAPTER XII

SOAPS AND MINERAL OIL EMULSIONS

SOAPS

Soaps are used alone to some extent in sprays for certain soft-bodied insects and in very large quantities in the preparation of oil emulsions and disinfectants. They are also used with other materials such as nicotine, quassia, etc., to cause them to spread and stick.

The soaps most commonly used are those made from fish oil with either sodium or potassium as the base and ordinary laundry soap. For the formation of emulsions potassium fish oil soap has been found the most satisfactory. For soap washes, or for mixing with nicotine or quassia, soda fish oil soap or even ordinary laundry soap is often used.

Preparation of Sample.—*Cake Soap.*—In the case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. With samples that cannot be handled in this way, quarter the cake by cutting at right angles in the center and shave equally from all fresh surfaces sufficient soap for analysis. Mix and weigh out promptly all portions for analysis. Preserve the remainder in an air-tight container in a cool place.

Liquid Soap.—No preparation other than thorough mixing is necessary.

Water.¹—Weigh about 20 grams of the sample into a 300-500 cc. flask; add 50 cc. of xylene and, to prevent foaming, add about 10 grams of lump rosin. (Do not use powdered rosin because it usually contains an appreciable quantity of moisture.) Distil into a Dean and Stark type distilling tube receiver² and continue the distillation until no more water collects in the receiver. Allow the contents of the tube to cool to room temperature, read the volume of water under the xylene in the tube, and from this volume calculate the percentage of water in the sample.

Sodium or Potassium Oxide.³—Weigh about 5 grams of the sample into a platinum dish and ignite until the soap is thoroughly charred. Leach with water and filter. Completely ash the filter and residue, take up with water, filter, and wash. Titrate the filtrate with standard acid, using methyl orange as the indicator. Make a qualitative flame test for sodium and potassium and calculate the percentage of the alkali in the sample as sodium or potassium oxide, as the case may be. If both sodium and potassium are present, determine the potassium by the platonic chloride method (*Methods of Analysis, A. O. A. C.*) and calculate the sodium oxide by difference.

¹ *J. Assoc. Official Agr. Chem.*, **9**, 28 (1926).

² See p. 490.

³ *J. Assoc. Official Agr. Chem.*, **10**, 157 (1927).

Unsaponified Fat or Oil.¹—Dissolve 10 grams of cake soap or 15 grams of liquid soap in 70–100 cc. of water and extract with 50–60 cc. of ether. If the two liquids do not separate, add a few cubic centimeters of alcohol. Separate the water solution and wash the ether with water made slightly alkaline with sodium hydroxide. Again successively extract the soap solution and washings with ether and evaporate the combined extracts to dryness in a weighed beaker, on a water bath. Since many of the hydrocarbon oils are volatile at 100° C. do not continue the drying any longer than necessary.

Fatty Anhydrides.—Transfer the aqueous solutions obtained in the preceding paragraph to a separatory funnel, acidify with hydrochloric or dilute sulfuric acid (1 + 3), extract 3 times with ether, and successively wash the ether extracts twice with water. Combine the ether extracts, evaporate in a weighed beaker on a steam bath, and weigh as fatty acids. From the weight of fatty acids calculate the percentage of soap in the sample as sodium or potassium oleate or the fatty anhydrides as oleic anhydride.

Glycerol.²—Dissolve an accurately weighed sample of the soap equivalent to not more than 3.0 grams of glycerol in 200 cc. of hot water in a 600 cc. beaker. Decompose with 25 cc. of sulfuric acid (1 + 3). If alcohol is present, volatilize it by boiling for 20–30 minutes. Cool, remove, and rinse the cake of fatty acids (if necessary paraffin may be added to make the fatty acids form a solid cake); transfer the acid water and rinsings to a 500 cc. volumetric flask, and add about 0.25 gram of silver sulfate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

Transfer a filtered, accurately measured 50 cc. aliquot of the above solution to a 400 cc. beaker, and add 75 cc. of accurately measured potassium dichromate solution (containing exactly 74.552 grams per liter) followed by 25 cc. of concentrated sulfuric acid (sp. gr. 1.84). Cover with a watch-glass, and oxidize by heating in a steam bath for 3 hours. Conduct a check experiment in like manner but use 100 cc. of water, 25 cc. of sulfuric acid (sp. gr. 1.84), and 25 cc. of accurately measured potassium dichromate.

Cool, and make up the solution to 1000 cc. in a volumetric flask. Determine the excess of potassium dichromate by taking a 50 cc. aliquot of the above, adding 50 cc. of water and 20 cc. of 10 per cent potassium iodide solution, and titrating the liberated iodine with 0.1 *N* thiosulfate, using starch solution as indicator. Calculate the percentage of glycerol (1 cc. of the potassium dichromate solution equals 0.0100 gram of glycerol). *Note.*—This method is not applicable in the presence of sugars or starch.

Free Alkali.—Dissolve a 10 gram sample in 200 cc. of freshly boiled ethyl alcohol of at least 94 per cent strength, neutral to phenolphthalein, and filter. Wash the residue on the filter paper with hot, neutral ethyl alcohol. Titrate the filtrate with standard acid, using phenolphthalein as indicator. Calculate the alkalinity to sodium or potassium hydroxide, as the case may be.

In the case of fish oil soaps it is sometimes desirable to check the source of the fat since fish oils vary to a considerable extent depending on the

¹ Adapted from *Methods of Analysis*, A. O. A. C., 1925, 295.

² *J. Ind. Eng. Chem.*, 14, 1163 (1922).

species of fish, season, place of catch, etc. All of them, however, that are of the type desirable for fish oil soaps are drying oils, that is, they have iodine numbers of from 130 to 200. Following are some iodine values given by A. R. Lange¹ as the average of a season's production:

Oil	Iodine number, Wijs
Crude menhaden oil	187
Winter-pressed menhaden oil	187.5
Herring oil	143
Crude sardine oil	178.5
Newfoundland cod oil	173

Lange states that tests run in his laboratory indicate that when in the Hanus method saturation is continued for 30 minutes, results approximately ten points lower than the iodine number (Wijs) will be obtained when the latter is 180. Holde² states that menhaden oil has an iodine number of 148-160. The iodine number may be determined by either the Hanus method³ or the Wijs method.³ For this determination the fatty acids separated in the determination of fatty anhydrides are used. The iodine number of the fatty acids is usually a little higher than that of the fat.

Rosin often occurs in laundry soap and a rosin fish oil soap is also prepared for some purposes. The rosin in such soaps may be determined by the method of Wolff.⁴

MINERAL OIL EMULSIONS

The oil emulsions used for insecticidal purposes consist of mineral oil dispersed in water with the aid of an emulsifier, which is usually soap. However, soap emulsions are liable to separate in the presence of hard water, and therefore numerous other emulsifiers have been used, among which are milk, lime-casein mixtures, glue, bentonite, dextrin and gums.

Kerosene emulsions were recommended for use against sucking insects by A. J. Cook⁵ in 1878. Later, distillate oils were used, and many proprietary products appeared on the market. The so-called "Government formula," which calls for the use of lubricating oil emulsified by the aid of fish oil soap, was suggested by W. W. Yothers⁶ in 1918 and recom-

¹ *J. Ind. Eng. Chem.*, **18**, 9 (1926).

² *Examination of Hydrocarbon Oils*. Trans. by Edward Mueller, 1915.

³ *Methods of Analysis*, A. O. A. C.

⁴ *J. Ind. Eng. Chem.*, **14**, 1161 (1922).

⁵ Rpt. Michigan State Board Agr., 1878, 434.

⁶ U. S. Dept. Agr. Farmer's Bull. **933**.

mended for use against San José scale by Ackerman¹ in 1923. Since then the use of oil emulsions has increased enormously and at present many millions of gallons are used annually.

Preparation of Sample.—Oil emulsions require no preparation except thorough mixing. In case of emulsions that cream out readily care must be taken to keep them mixed during the weighing out of the portions for analysis.

Water.²—Weigh about 25 grams of the sample into a 300-500 cc. flask; add 50 cc. of xylene and, to prevent foaming, add a small piece of rosin. Distil into a Dean and Stark type distilling tube receiver³ and continue the distillation until no more water collects in the receiver. Allow the contents of the tube to cool to room temperature, read the volume of the water under the xylene in the tube, and from this volume calculate the percentage of water in the sample. This method is applicable to practically all oil emulsions and miscible oils except a few of the latter that contain small quantities of alcohol.

Sodium and Potassium Oxides.—Use the same method as described under soaps.

Total Oil.²—Weigh about 10 grams of the sample into a Babcock cream bottle. Dilute with about 10 cc. of hot water and add 5-10 cc. of dilute sulfuric acid (1 + 1). Set the bottle in a hot water bath for about 5 minutes to hasten the separation of the oil, add sufficient saturated sodium chloride solution to bring the oil layer within the graduations on the neck of the bottle, whirl at a rate of 1200 revolutions per minute for 5 minutes, and allow to cool. Read the volume of the oil layer, determine its specific gravity, and from these values calculate its weight and percentage. From this percentage value deduct the percentage of fatty acids determined separately, to obtain the percentage of oil in the sample.

This method is applicable to emulsions containing all fractions of mineral oil from gasoline to lubricating oil. It is applicable in the presence of soap as an emulsifier but not in the presence of gums, casein, dextrin, or other insoluble emulsifiers.

In the presence of casein and some gums it is possible to determine the oil by breaking down the emulsifier with commercial concentrated sulfuric acid and determining the oil as in the Babcock method⁴ for fat in cream, the quantity of sample and method of calculation being the same as in the method for oil already described.

In the presence of mineral emulsifiers it is sometimes possible to distil off the water, separating the oil which goes over with the water and returning it to the distillation flask, and then extract the oil from the emulsifier with ether. The ether is carefully evaporated, and the residual oil is weighed.

Soap.²—Weigh 20 grams of the sample into a separatory funnel, add 60 cc. of petroleum ether, and extract the mixture once with 20 cc. and four times with 10

¹ U. S. Dept. Agr. Circ. 263.

² J. Assoc. Official Agr. Chem., 9, 28 (1926).

³ See p. 490.

⁴ Methods of Analysis, A. O. A. C.

cc. of 50 per cent alcohol. Break the emulsion if necessary with 1 or 2 cc. of a strong solution of sodium hydroxide, allowing the solution to run down the side of the separatory funnel, which is then gently twirled and allowed to stand for a few minutes. Draw off the alcoholic layers and wash them successively through petroleum ether contained in two other separatory funnels. Combine the alcoholic extracts in a beaker and evaporate on a steam bath to remove the alcohol. Dissolve the residue in about 100 cc of water made alkaline with sodium hydroxide. Transfer to a separatory funnel, acidify with hydrochloric or sulfuric acid, extract three times with ether, and wash the ether extracts twice with water. Combine the ether extracts, evaporate in a weighed beaker on a steam bath, and weigh as fatty acids. From the weight of fatty acids calculate the percentage of soap in the sample as sodium or potassium oleate.

This method is not applicable in the presence of phenols. If phenols are present the method may be modified by adding sufficient 25 per cent sodium hydroxide solution to the 50 per cent alcohol used to extract the soap from the petroleum ether-oil solution so that all the phenols will be dissolved in the alcoholic layer. The alcohol is then evaporated off, and the soap and sodium phenates are dissolved in water and transferred to a 500 cc. Kjeldahl flask. Sulfuric acid (1 + 3) is added to free the phenols and fatty acids and the mixture is steam distilled until no more phenols come over. The fatty acids are extracted with ether, determined and calculated to sodium or potassium oleate as previously described. The aqueous distillate is saturated with salt and extracted with three 40 cc. portions of ether, the ether extracts are combined in a tared beaker, the ether is carefully evaporated, and the phenols that remain are weighed. In evaporating the ether from the phenols it is well to remove the last traces by means of a gentle air blast. The lower boiling phenols are somewhat volatile and the evaporation should not be continued any longer than necessary.

Insoluble Emulsifiers.—Owing to the number of emulsifiers of this type and their lesser relative importance the analysis of emulsions prepared with them has been less carefully studied than in the case of the soap emulsions. However, two methods have been used, and they appear to be quite generally applicable. In one 5–10 grams of the emulsion is diluted with an equal mixture of absolute alcohol and anhydrous ether until there is no separation into layers; the mixture is filtered through a tared filter; the filter and its contents are washed with the mixture of alcohol and ether and then several times with ether, and dried to constant weight. In the other method, after the determination of water by the xylene distillation method, the emulsifier will be found to have separated in the distillation flask. It is transferred to a tared filter by the aid of ether and a stirring rod, washed with ether, dried, and weighed as already described. In using this latter method it is sometimes found that the emulsifier is sticky and hard to remove from the distillation flask; at other times it has been found that the emulsifier occludes some of the oil and produces results somewhat high. In the first method, particularly if the oil is high boiling and a high percentage of water is present, it is sometimes difficult to get all the oil and water to dissolve in the solvents without using excessive quantities of them. In such cases it is sometimes possible first to get rid of most of the water by adding a larger proportion of absolute alcohol and pouring the top

layer through the filter, adding more anhydrous ether to dissolve the oil, and proceeding as suggested.

Testing the Oils.—In the case of the lubricating-oil emulsions it is often necessary to determine the properties of the oil. This is particularly desirable because there is considerable experimental evidence that the unsaturated oils are much more likely to injure foliage than are the saturated oils. The tests usually made are as follows:

Specific Gravity.—Determine at 20° C. by means of a Westphal balance.

Flash Point and Fire Point.—Determine by means of the Cleveland open cup tester, A. S. T. M. Method D 92-24, which is described in detail in U. S. Bur. Mines Tech. Paper 323 B.

Volatility.—Weigh approximately 20 grams of the oil into a tared crystallizing dish $3\frac{1}{2}$ inches in diameter, heat the dish and contents in a constant temperature oven at 105° C. for 4 hours, and determine the loss of weight. If a considerable quantity of volatile oil, such as gasoline, is known to be present, heat the oil for the first hour on the water bath in order to avoid danger of explosion. The type of lubricating oil commonly used in such emulsions, however, is not sufficiently volatile to cause any danger in putting it directly into an electric oven at 105° C.

Viscosity.—Determine viscosity at 100° F. by means of the Saybolt Universal viscosimeter by A. S. T. M. Method D 88-26.

Solidification.—To test the effect of temperature on the oil determine the cloud and pour points by A. S. T. M. method D 97-27 T, which is described in U. S. Bur. Mines Tech. Paper 323 B. For some purposes it may be sufficient to cool the oil in a test tube immersed in a salt and ice bath to -5° C. for several minutes and note its solidity or fluidity at that temperature.

Un sulfonated Residue.—This determination is considered the most important indication of the proportion of unsaturated compounds in the oil and thus the most important indication of the probability of foliage injury. The method follows.

With a pipet measure 5 cc. of the oil into a Babcock cream bottle. After preliminary draining, in the case of heavy oils, to reduce the viscosity warm the pipet by drawing it several times through the flame of a Bunsen burner and then drain thoroughly. If greater accuracy is desired, the measured charge may be weighed and its exact volume calculated from the weight and specific gravity of the oil. Use a bottle about 15 cm. long—either the 9 gram 50 per cent or the 18 gram 30 per cent cream bottle. Add slowly 20 cc. of the 38 *N* fuming sulfuric acid, gently shaking or rotating the bottle and taking care that the temperature does not rise above 60° C., by cooling in ice water if necessary. When the mixture no longer develops heat on shaking, agitate thoroughly, place the bottle in a water bath, and heat at 60°-65° C. for 10 minutes, keeping the contents of the bottle thoroughly mixed by shaking vigorously for a period of 20 seconds at 2 minute intervals. Remove from the bath and fill the bottle with concentrated sulfuric acid until the oil rises into the graduated neck. Centrifugalize for 5 minutes (or longer if necessary to obtain a constant volume of the oil) at 1200-1500 revolutions per minute. Read the volume of unsulfonated residue from the graduations on the neck of the bottle, and from this reading calculate the percentage by volume of the unsulfonated oil.

CHAPTER XIII

PLANT PRODUCTS

Many plants, or products derived from them, have been suggested as having insecticidal properties. McIndoo and Sievers¹ published a list of 260 species of such plants and also tested many of the plants. They concluded that of the 260 plants listed, only about 5 per cent furnishes material for effective insecticides, of which only about half has attained any considerable use.

PYRETHRUM POWDER (INSECT POWDER—PERSIAN INSECT POWDER)²

Pyrethrum or "insect powder" consists of the powdered flower heads of certain species of chrysanthemum, the one most commonly used being *Chrysanthemum cinerariaefolium*. The Food and Drug Administration of the United States Department of Agriculture recognizes³ as insect powder an insecticide made from the powdered flower heads of the following species of chrysanthemum:

1. *Chrysanthemum (Pyrethrum) cinerariaefolium* (Trev.) Bocc.
2. *Chrysanthemum (Pyrethrum) roscum* Web. and Mohr.
3. *Chrysanthemum marshallii* Aschers. (synonym, *Pyrethrum roscum* Bieb.)

Pyrethrum powder has been in use for more than a century and is a very important insecticide. The importation of insect flowers into the United States during 1928 amounted to eleven million pounds, the principal sources of supply being Dalmatia and Japan.

Many substances have been used to adulterate insect powder. Bulletin 824, cited above, lists more than fifty materials that have been used for this purpose. In addition to the powdered stems of the pyrethrum plant, which has been the most extensively used adulterant, the following adulterants have been detected in the Insecticide and Fungicide Laboratory of the Food and Drug Administration: lead chromate, potassium chromate, barium chromate, turmeric, sand, leaves of the pyrethrum plant, and ox-eye daisy flowers (*Chrysanthemum leucanthemum*).

¹ U. S. Dept. Agr. Bull., 1201.

² Much of the information here given is taken from U. S. Dept. Agr. Bull. 824, by McDonnell, Roark, LaForge and Keenan.

³ Insecticide Decision 1. U. S. Dept. Agr., Office Secretary, Aug. 26, 1911.

The presence of other plant tissues cannot be demonstrated satisfactorily by chemical means, and examination by an experienced microanalyst is essential. The microscopic examination of pyrethrum is treated fully in the bulletin cited. Certain chemical determinations are usually made to supplement the work of the microanalyst. These include moisture, nitrogen, ether extract, ash, and acid-insoluble ash.

Moisture.—Weigh 2 grams of the powder in a previously dried and weighed moisture dish. Place the cover on very lightly and dry the sample in a water-jacketed vacuum oven at a pressure of 5–7 inches of mercury for 5 hours. Cool the dish and contents in a desiccator and weigh immediately. Report the percentage loss in weight as moisture.

Ether Extract

Reagent.—*Anhydrous ether.*—Wash commercial ether with two or three successive portions of water, add solid sodium or potassium hydroxide, and allow to stand until most of the water has been abstracted from the ether. Decant into a dry bottle, add small pieces of carefully cleaned metallic sodium, and let stand until there is no further evolution of hydrogen gas. Keep the ether, thus dehydrated, over metallic sodium in loosely stoppered bottles.

DETERMINATION

Transfer the residue from the moisture determination to a Knorr, Soxhlet or other extraction apparatus, the flask of which has been dried and weighed. Pour about 30 cc. of anhydrous ether into the flask and extract the sample for 16 hours, using a heating element not above 100° C. Note the color of the extract at this point.

When the extraction is finished, remove the extraction thimble and replace it with a receptacle for recovering the ether if the extraction apparatus used is of a type to permit this procedure. Distil the ether from the residue; remove the flask from the apparatus; dry for an hour at 100° C., preferably in a vacuum oven; cool in a desiccator and weigh. Calculate and report the increase in weight of the flask as percentage of ether extract.

Ash.—Weigh 5 grams of the sample in a weighed platinum dish and ignite at a dull red heat in a muffle until most of the carbon is burned off and the ash has developed a gray color. Remove the dish from the muffle and pulverize the ash with a glass rod flattened on the end. Return the dish to the muffle and heat for 15–20 minutes or until the last traces of carbon have been burned off. Remove the dish from the muffle, cool in a desiccator, and weigh immediately. Report the percentage of residue as ash.

Acid-Insoluble Ash.—Boil the ash with 100 cc. of dilute hydrochloric acid (1 + 4) for 15 minutes, filter, and wash. Ignite the residue, weigh, and report the percentage of residue as acid-insoluble ash.

Nitrogen.—Determine by the Kjeldahl-Gunning-Arnold method, as described under fertilizers, using 2 grams of the powder for each determination.

Interpretation of the Analytical Results.—McDonnell, Roark, LaForge and Keenan report analyses of pure insect powder by the methods outlined above. They report the following percentages for powders made from "closed" and "open" flowers: *Closed flowers*, nitrogen 1.5 to 2.0, ether extract 6.0 to 7.5, ash 6.0 to 8.5, ash insoluble in hydrochloric acid 0.08 to 2.0; *open flowers*, nitrogen 1.2 to 1.4, ether extract 5.0 to 7.0, ash 5.0 to 7.0, ash insoluble in hydrochloric acid 0.08 to 0.65.

In the analysis of insect powder the results should come within those just quoted. A low percentage of nitrogen is a basis for suspicion that the powder has been made from low-grade flowers or that powdered stems have been added to it. The color of the ether extract also gives an indication of the presence of powdered stems. The color of this extract from a pure pyrethrum powder is yellow, and a distinct green color is a positive indication of the presence of stem powder or other adulterant.

A low value for the ether extract may indicate that the sample contains powder that has been exhausted of its active principle in the manufacture of pyrethrum extract insecticides.

The insoluble ash usually is less than 1.0 per cent and should never exceed 2 per cent.

Active Principles of Pyrethrum.—It is only recently that the active constituents of pyrethrum have been isolated and identified by Staudinger and Ruzicka.¹ The active principles consist of two closely related complicated esters to which the names Pyrethrin I and Pyrethrin II² have been given and which have the formulas given on p. 570.

Staudinger and Harder³ were the first to develop methods for the determination of the pyrethrin content. They proposed two procedures, one consisting of the isolation, separation and titration of the corresponding mono- and dicarboxylic acids, the other being based upon the determination of nitrogen in the crude semicarbazone formed by treating a methyl alcoholic extract with semi-carbazide and acetic acid. Tattersfield, Hobson and Gimingham⁴ modified these methods by shortening the procedure

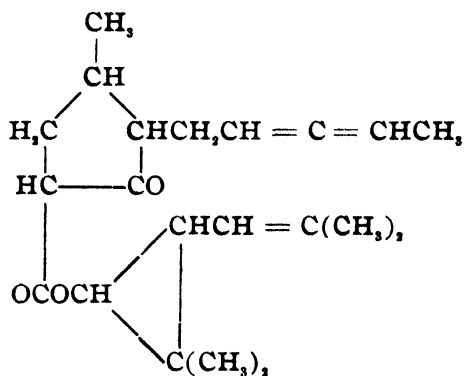
¹ *Helv. Chim. Acta.*, **7**, 177-259, 377-458 (1924).

² Ott and Behr, *Ber.*, **60** B, 2284-7 (1927), have called attention to the fact that the name "Pyrethrin" has long been used to designate the active principle of *Radix pyrethri*, which is the powdered root of *anacyolus pyrethrum* (Linné) de Candolle, and consider that Staudinger and Ruzicka should not have used this term for the constituents of insect powder. In this chapter the terminology of Staudinger and Ruzicka has been followed because it has been used by all recent investigators of *Chrysanthemum cinerariaefolium*.

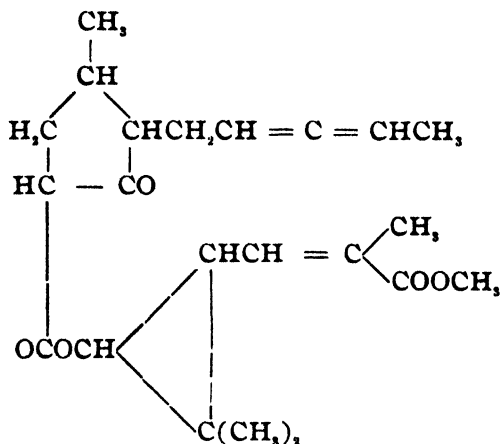
³ *Ann. acad. sci. Fennicae, Ser. A*, **29**, No. 18, 1-14.

⁴ *J. Agr. Sci.*, **19**, part 2, 266 (1929).

PYRETHRIN I



PYRETHRIN II



and using a much smaller quantity of sample. They proved that there is a close correlation between the results obtained by these methods and the toxicity of the samples when tested biologically.

The total pyrethrin content of the powders from Dalmatia, Switzerland and elsewhere examined by Staudinger and Harder varied between 0.25 and 0.61 per cent. Tattersfield, Hobson and Gimingham found from 0.59 to 1.29 per cent total pyrethrin in their samples, which were prepared from flowers grown at various British experiment stations.

The following are the modified methods used by Tattersfield, Hobson and Gimingham.

Acid Method.—Extract 10 grams of the ground flower heads or 50 grams of the stalk with low-boiling petroleum ether (boiling range below 40° C.) in a Soxhlet extractor heated over a carbon-filament lamp. When extraction is complete, evaporate the petroleum ether to small bulk in a rapid current of carbon dioxide with gentle warming and complete the evaporation in a vacuum desiccator. Extract the residue successively with four (or in the case of the stalk powder, six) 2.5 cc. portions of absolute methyl alcohol (free from acid), warming each on the water bath. Cool each extraction under the tap, filter through a small wad of fat-free absorbent cotton into a long-neck flask of 100 cc. capacity, and finally rinse the extraction flask with 2.5 cc. of cold methyl alcohol. Treat the clear solution with 4 cc. of normal sodium hydroxide in methyl alcohol, and boil under a reflux condenser for 6-8 hours, after which evaporate the methyl alcohol under vacuum with gentle warming. Use a right-angle tube connection between the condenser and flask to prevent spray from being carried over. Do not allow the temperature to rise so high that the alcohol condenses in the connecting tube. Rinse the stopper and connecting tube, catching the rinsings in the flask, add a little water to bring the soaps into solution, add 6 cc. of normal sulfuric acid, and distil the acid liquid with steam. (Tattersfield, Hobson and Gimingham used a distillation apparatus similar to the original Pregl micro-Kjeldahl still,¹ except that the rubber connection with the condenser was eliminated so that the glass tube connected directly with a small worm condenser and led to a receiver marked at the 50 cc. level.) Collect 50 cc. of distillate for the determination of volatile acid and then continue the distillation until a further 100 cc. has been collected. Transfer the first 50 cc. distillate to a pear-shaped separatory funnel and extract twice with 50 cc. of low-boiling petroleum ether, which can be conveniently measured out in the receiver. Shake vigorously during the extraction, and wash each extract with a small quantity of water. Add 20 cc. of water to the combined extracts, gently evaporate the petroleum ether, and titrate the residue with 0.02 *N* sodium hydroxide solution. Use phenolphthalein indicator and continue the titration to a distinct pink, which persists for at least 1 minute after shaking. (The acid tends to adhere to the sides of the flask, and it is necessary to wash it down with neutralized alcohol.) Calculate the percentage of pyrethrin I on the basis that 1 cc. of 0.02 *N* sodium hydroxide solution equals 6.60 mg. of that compound.

To the hot residue in the flask, which should not exceed 40 cc., add 0.2 gram of pure calcium sulfate and let stand overnight in order to clarify the solution. Filter the solution into an automatic extractor, using a small wad of cotton, just sufficient to give a gentle flow and produce a clear filtrate. Extract with acid-free ethyl ether for 8 hours, after which add 20 cc. of water to the ether extract and gently distil off the ether. Finally, filter the aqueous layer through a loosely packed wad of fat-free cotton, and titrate the dicarboxylic acid with 0.02 *N* sodium hydroxide solution. Calculate the percentage of pyrethrin II on the basis that 1 cc. of 0.02 *N* alkali equals 3.74 mg. of the pyrethrin.

Semicarbazone Method.—Completely extract 10 grams of the powdered flower-heads with low-boiling petroleum ether, evaporate the solvent, and extract the residue from it with absolute methyl alcohol exactly as in the acid method. Filter the

¹Quantitative Organic Micro-Analysis, 96 (1924).

extracts successively into a small measuring cylinder and adjust to a volume of 10 cc. Mix the solution and pipet 4 cc. aliquots into hard-glass test tubes, add 30 mg. of semicarbazide hydrochloride and 50 mg. of sodium acetate, and concentrate the solution to about 0.5 cc. by inserting a rubber stopper having a capillary tube reaching to the bottom of the liquid and a side tube connected to a pump, after which the test tube is maintained at 25° C. and the alcohol removed by evacuation. The side tube should contain a spray trap consisting of a glass bead held in position between two constrictions. When the distillation is finished, pour a few drops of methyl alcohol into the side tube and so manipulate the apparatus as to wash down both the side tube and capillary tube in order to free them from any deposit carried up by the spray. Cork the test tube and place it in a bath at 25° C. for 36-48 hours. Then evaporate the methyl alcohol to dryness by connecting to a pump and evacuating without the use of a capillary. To remove the excess of semicarbazide two methods of washing may be employed:

(a) Add a little ether to the residue and then evaporate to a film by tilting and rotating the test tube, keeping it from cooling by warming with the hand. Remove the last traces of ether with a good vacuum. (The film should cover half the length of the test tube.) Carefully pour a solution containing 0.1 per cent acetic acid and 1 per cent sodium acetate into the tube so that the film is completely covered and allow to stand for 10 minutes. Then filter the solution through a small plug of cotton and rinse the test tube with about 2 cc. of water. Next dissolve the film in ether, redeposit it by evaporation of the ether, and again wash. Carry out this process three times. Return the small residue remaining on the filter to the test tube by pouring through it 2 drops of methyl alcohol and 1 cc. of ether. Evaporate the alcohol and ether in vacuo. Heat 5 cc. of a 15 per cent hydrochloric acid solution containing 5 per cent of mercuric chloride and pour through the filter into the test tube.

(b) The alternative and more rapid method of washing is as follows: After complete removal of the methyl alcohol, extract the residue twice with 5 cc. of ether and pour the ether solution into a small separatory funnel. Wash the residue in the test tube four times with 10 cc. of water and filter the washings successively through a cotton plug into the separatory funnel. Wash the ether solution with each of these washings by gently rotating the funnel, then wash it twice more with portions of water, return it to the test tube, and evaporate off the ether. Heat 5 cc. of the 15 per cent hydrochloric acid solution containing 5 per cent of mercuric chloride, and after loosening the cotton plug use this solution to wash into the test tube the insoluble material left in the separatory funnel and the filter.

From this point the procedure is the same in both (a) and (b). Connect the test tube to a small reflux condenser, add a little pumice, and boil the solution for 7 hours. Then determine ammonia according to the procedure adopted by Pregl in his revised micro-Kjeldahl method (*loc. cit.*).

Prepare the reagent used in this determination to render the contents of the flask alkaline, by diluting a 40 per cent solution of sodium hydroxide with an equal volume of a saturated solution of sodium thiosulfate. The latter is necessary for the decomposition of the mercury ammonium complex. Use 0.02 *N* acid to absorb the ammonia and 0.02 *N* alkali for titration.

The mixed pyrethrins are present in nearly equal proportions and 350 may be taken as the mean molecular weight. Calculate their percentage on the basis that 1 cc. of 0.02 *N* acid is equivalent to 7.0 mg. of the combined pyrethrins.

Tattersfield, Hobson and Gimmingham commenting on the relative value of the two methods make the following statement:

Whereas the acid method has presented no great difficulty in adapting to a small scale technique, the determination of the pyrethrin content by means of the semicarbazone required considerable modification. Moreover, the procedure is tedious and gives only an approximate estimation of the sum of the two pyrethrins, and as pyrethrin I is the main toxic constituent of pyrethrum, there is some objection to its use for practical purposes; we have, therefore, only used it to confirm that the amounts of the acids are a true measure of the pyrethrin content.

Tattersfield and Hobson¹ have further modified the method for pyrethrin I and claim that the results obtained by this more rapid procedure approximate those obtained by the longer method.

For the determination of total pyrethrins Gnadinger and Corl² propose the following copper reduction method, which is based on the method of Folin³ for the determination of dextrose in blood.

REAGENTS

(a) *Petroleum ether*.—90–99 per cent distilling between 20 and 40°; maximum boiling point, 60°.

(b) *Aldehyde-free alcohol*.—Allow 95 per cent alcohol, containing 5 grams of *m*-phenylene-diamine hydrochloride per liter, to stand for 24 hours with frequent shaking. Boil under a reflux condenser for at least 8 hours, allow to stand overnight and distil, rejecting the first 10 and the last 5 per cent of distillate. Store in a dark place in well-filled bottles.

(c) *Basic lead acetate solution*.—Dissolve 20 grams of Horne's basic lead acetate in sufficient recently boiled water to make 1 liter.

(d) *Alkaline copper solution*.—Dissolve 2.5 grams of purest copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in about 100 cc. of water, warming gently; cool when dissolved. Dissolve 5 grams of highest purity sodium potassium tartrate and 7.5 grams of purest sodium hydroxide separately in about 100 cc. of cold water. Transfer the solutions to a 500 cc. volumetric flask, mix and dilute to the mark. (This solution should not be used after it is three days old.)

(e) *Folin's reagent*.—Dissolve 150 grams of sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, in 300 cc. of water. Filter through a 15 cm. quantitative filter paper into a 1 liter

¹ *J. Agr. Science*, **19**, 433–437 (1929).

² *J. Am. Chem. Soc.*, **51**, 3054–64 (1929).

³ *J. Biol. Chem.*, **87**, 357–370 (1926).

flask and wash with 75 cc. of water. Add 0.1–0.2 cc. of bromine and shake until the bromine is dissolved. Let stand for one hour, then add with shaking 225 cc. of 85 per cent phosphoric acid. Add 150 cc. of sulfuric acid (1 volume of concentrated acid mixed with 3 volumes of water and cooled). Remove the liberated bromine by means of a moderately rapid current of air (the aeration requires about 30 minutes). Finally add 75 cc. of 99 per cent acetic acid, mix and dilute to a volume of 1 liter.

(f) *Standard dextrose solution*.—Dissolve exactly 1 gram of pure anhydrous dextrose in water and transfer to a 200 cc. volumetric flask. Add 40 cc. of aldehyde-free alcohol, mix and dilute to 200 cc. with water. Transfer 10 cc. of this solution to a 250 cc. volumetric flask by means of a pipet, add 210 cc. of aldehyde-free alcohol and dilute to 250 cc. with water; 10 cc. of this dilute solution contains 2 mg. of dextrose. The strong solution is stable for months; the dilute solution should be made fresh each week.

APPARATUS

(a) *Constant-temperature water bath*.—Set at 78° C., corrected, and controlled within $\pm 0.2^\circ$.

(b) *Colorimeter*.—Duboscq or Klett type, with artificial illuminator.

(c) *Folin sugar tubes*.¹—Blown to contain 15.5 cc. to base of constriction. When heated to 78° C. the surface of the liquid must fall within the constricted portion of the tube. The internal diameter of the constricted portion should be the same for all tubes in a set.

DETERMINATION

Extract 20 grams of ground Pyrethrum flowers (about 30-mesh) for 5 hours with petroleum ether in a Soxhlet extractor. Cool the petroleum ether solution to about 20° and let stand for at least 30 minutes. Filter through a quantitative filter paper into a 400 cc. beaker, add a few grains of ignited sand and evaporate at a temperature not exceeding 75° C. As soon as the last traces of petroleum ether are driven off, transfer the residue with five or six portions of boiling 95 per cent aldehyde-free alcohol to a 100 cc. volumetric flask (previously marked at the 80-cc. point), using sufficient boiling alcohol to make the volume 80–85 cc. To the hot solution add from a pipet 15 cc. of basic lead acetate solution and make to the mark with hot alcohol. Shake vigorously, cool at once to 20° and again make to the mark with alcohol. Filter and to the filtrate add about 1 gram of anhydrous sodium carbonate. Let stand for 15–20 minutes, shaking frequently, and filter. Immediately pipet 10 cc. of the clear filtrate into a Folin tube and add, also from a pipet, 6 cc. of alkaline copper solution. Mix thoroughly, keeping the solution in the bulb of the tube. Measure 10 cc. of standard dextrose solution (2 mg. of dextrose) with a pipet into a second tube and add 6 cc. of copper solution. Place the tubes upright in the constant-temperature bath, set at 78° corrected, and heat for exactly 45 minutes. Remove from the bath and place in water at 20° for 3 minutes. Add 10 cc. of Folin's reagent, from a pipet, and let stand for 3 minutes; then stopper the tubes, mix thoroughly, transfer to 100 cc. volumetric flasks and make to the

¹ *J. Biol. Chem.*, 41, 372 (1920).

mark with water. Filter through a Gooch crucible fitted with a heavy asbestos pad, using gentle suction. Do not use filter paper. The dextrose solution need not be filtered. Compare the solutions at once in the colorimeter and from the readings calculate the dextrose equivalent to the unknown solution in the usual way. Reference to Col. 3 of Table II will give the amount of pyrethrins, in milligrams, equivalent

TABLE II.—COPPER REDUCING POWER OF DEXTROSE AND PYRETHRINS.*

Dextrose, mg.	Pyrethrin I, mg.	Pyrethrin I and II, mg.	Dextrose, mg.	Pyrethrin I, mg.	Pyrethrin I and II, mg.	Dextrose, mg.	Pyrethrin I, mg.	Pyrethrin I and II, mg.
0.750	4.87	5.19	1.475	9.07	9.68	2.200	14.31	15.26
0.775	5.01	5.34	1.500	9.23	9.85	2.225	14.52	15.49
0.800	5.14	5.48	1.525	9.39	10.02	2.250	14.73	15.71
0.825	5.28	5.63	1.550	9.55	10.19	2.275	14.95	15.94
0.850	5.41	5.77	1.575	9.72	10.37	2.300	15.17	16.18
0.875	5.55	5.92	1.600	9.88	10.54	2.325	15.40	16.42
0.900	5.69	6.07	1.625	10.04	10.71	2.350	15.62	16.66
0.925	5.82	6.21	2.100	13.40	14.39	2.825	20.80	22.28
0.950	5.96	6.36	1.650	10.21	10.89	2.375	15.85	16.91
0.975	6.10	6.51	1.675	10.38	11.07	2.400	16.09	17.16
1.000	6.24	6.66	1.700	10.55	11.25	2.425	16.33	17.42
1.025	6.38	6.81	1.725	10.72	11.43	2.450	16.57	17.68
1.050	6.52	6.95	1.750	10.89	11.62	2.475	16.81	17.93
1.075	6.67	7.11	1.775	11.07	11.81	2.500	17.05	18.19
1.100	6.81	7.26	1.800	11.24	11.99	2.525	17.31	18.40
1.125	6.95	7.41	1.825	11.42	12.18	2.550	17.58	18.75
1.150	7.10	7.57	1.850	11.60	12.37	2.575	17.85	19.04
1.175	7.25	7.73	1.875	11.78	12.57	2.600	18.11	19.32
1.200	7.39	7.88	1.900	11.96	12.76	2.625	18.38	19.61
1.225	7.54	8.04	1.925	12.15	12.96	2.650	18.67	19.91
1.250	7.69	8.20	1.950	12.33	13.15	2.675	18.95	20.21
1.275	7.84	8.36	1.975	12.52	13.35	2.700	19.25	20.53
1.300	7.99	8.52	2.000	12.71	13.56	2.725	19.56	20.86
1.325	8.14	8.68	2.025	12.90	13.76	2.750	19.86	21.18
1.350	8.29	8.84	2.050	13.10	13.97	2.775	20.20	21.55
1.375	8.44	9.00	2.075	13.30	14.19	2.800	20.55	21.92
1.400	8.60	9.17	2.125	13.69	14.60	2.850	21.24	22.65
1.425	8.76	9.34	2.150	13.90	14.82	2.875	21.59	23.03
1.450	8.92	9.51	2.175	14.11	15.05			

* Third column calculated for a mixture of equal parts of pyrethrin I and II.

lent to the dextrose found in the unknown solution, or milligrams of pyrethrins in the 2 gram aliquot of flowers taken.

Gnadinger and Corl make the following comments on their method:

Blank determinations were run several times each day, or with nearly every set of tests. No difficulty was experienced in obtaining blanks equivalent to 0.05 mg. of dextrose, and for this reason no correction for the blank was made in calculating Table II. Reagents that yield a blank equivalent to more than 0.10 mg. of dextrose should be rejected. High blanks may be due to impurities in any of the reagents, but the sodium potassium tartrate, sodium molybdate and aldehyde-free alcohol especially

should be carefully tested. If the blank is between 0.05 and 0.10 mg. of dextrose, when compared with the standard dextrose solution, the error due to the blank is negligible.

The petroleum ether extract should not be heated longer than necessary to drive off the solvent. Generally only 5 or 10 minutes' heating above 60° will be required if the petroleum ether meets the specifications given. High-boiling petroleum ether should not be used.

The proportion of alcohol and water in the contents of the Folin tubes is carefully adjusted; if more alcohol is used the copper salts will be precipitated; if the percentage of water is increased the pyrethrins will be thrown out of solution. In either case incorrect results will be obtained. The Folin tubes should be dried before using, and the measurements should be made with pipets. Smaller aliquots than 10 cc. can be used for a determination, but sufficient aldehyde-free alcohol (80.5 per cent) must be added to the tube to make the total volume of the pyrethrin solution 10 cc. Larger aliquots than 10 cc. cannot be used.

It is essential that the bath be maintained at 78° corrected, $\pm 0.2^\circ$, and a stirrer should be provided to insure even temperature and circulation around the tubes, which should be immersed to a depth of 8–10 cm. Variations in time of heating or in temperature will yield results that are not comparable with Table II. After removing the tubes from the bath they should be treated as nearly alike as possible; therefore it is inadvisable to run more than 3 or 4 tubes at a time.

In making the color comparisons the standard dextrose is set at 20 mm. The unknown will then read between 14 and 50 mm. for quantities between 23 and 5 mg. of pyrethrins. If the reading is less than 12 mm., the entire amount of copper may have been reduced, and the determination should be repeated with a smaller aliquot. It is also desirable, if the reading is more than 40 mm., to run a duplicate determination using 40 grams of flowers instead of 20.

PYRETHRUM EXTRACTS

The lighter fractions distilled from mineral oil easily extract the active principles from pyrethrum, and recently large quantities of such extracts have been placed on the market. In addition to these mineral oil extracts there are also concentrated alcoholic extracts, sometimes referred to as "oleoresins," and pyrethrum soaps.

At present there are no satisfactory chemical methods for analyzing these products; they are evaluated by practical tests against flies or other insects.

It is possible that the methods described under "Pyrethrum Powder" may be adapted to the determination of the active principle in such products, but as yet this has not been done.¹

TOBACCO AND ITS PRODUCTS

Tobacco is another plant that furnishes valuable insecticides, the active principle being the alkaloid nicotine. Large quantities of tobacco are used

¹ Since this manuscript has been prepared such an adoption has been suggested by Vollmar, *Ind. Eng. Chem. Anal. Ed.*, **3**, 110 (1931).

in powder form, especially in the preparation of louse powders and also to a considerable extent for use on plants. However, the largest use of tobacco in the insecticide industry is for the preparation of concentrated solutions of nicotine. These solutions are of two types, one containing free nicotine and the other nicotine sulfate. The commercial products of both types are usually prepared to contain 40 per cent of the alkaloid. The so-called nicotine dusts are made by mixing free nicotine or nicotine sulfate solutions with dry carriers, such as infusorial earth, sulfur, gypsum, etc.

The best method for the determination of nicotine is the silicotungstic acid method,¹ in which the nicotine is steam distilled from a portion of the thoroughly mixed sample made alkaline with sodium hydroxide solution. The distillate is slightly acidified with hydrochloric acid, and the nicotine is precipitated with silicotungstic acid solution. The precipitate is filtered off, washed, ignited and weighed as silicotungstic oxide, from which the percentage of nicotine is calculated.

In tobacco powders the ash and acid-insoluble ash may be determined by the methods described under "Pyrethrum Powder."

HELLEBORE

This material, which is the powdered roots of *Veratrum album* or *Veratrum viride*, is used as a stomach poison for the control of certain insects, notably the currant worm. The active principles are alkaloids. During 1928 the imports of hellebore into the United States amounted to 700,000 pounds. The plants grow in certain parts of the United States, but very little is obtained commercially from this source.

Moisture, Ash, Acid-Insoluble Ash.—Proceed as directed under "Pyrethrum Powder," p. 568.

Total Alkaloids

REAGENTS

(a) *Chloroform-ether mixture.*—Mix 1 volume of chloroform with 2 volumes of ethyl ether.

(b) *Dilute ammonia.*—Dilute 10 cc. of concentrated ammonium hydroxide to 100 cc. with dilute water.

(c) *Dilute acetic acid.*—Dilute 2 cc. of glacial acetic acid to 100 cc. with distilled water, add 10 cc. of ethyl ether, shake in a separatory funnel, and draw off the lower layer for use.

¹ *Methods of Analysis, A. O. A. C.*

(d) *Dilute hydrochloric acid*.—Dilute 10 cc. of strong hydrochloric acid to 1 liter.

DETERMINATION

Place 15 grams of the well-mixed powdered hellebore in a dry, glass-stoppered Erlenmeyer flask of 300 cc. capacity. Add 150 cc. of the chloroform-ether mixture, stopper, shake well, and allow to stand 10 minutes. Add 5 cc. of the dilute ammonia water and shake vigorously every 10 minutes for 2 hours. Add 15 cc. of water, shake, and allow the powder to coagulate; decant the supernatant liquid through cotton, collect exactly 100 cc., and evaporate nearly to dryness in a beaker on the water bath.

Digest the residue in the beaker with 20 cc. of the dilute acetic acid, and transfer to a separatory funnel with the aid of a little water and about 20 cc. of ether. Shake thoroughly and collect the aqueous layer in another separatory funnel. Continue the extraction with 2 additional portions of acetic acid, 2 of hydrochloric acid and 1 of water, using about 20 cc. each time. Wash the combined aqueous solutions with 10 cc. of ether, separate carefully into the beaker used for the evaporation, warm gently to drive off the ether, filter if necessary, and collect the filtrate in a separatory funnel.

Precipitate the alkaloids with ammonia and extract them from the mixture by means of chloroform (3 portions of 20 cc. are usually sufficient).

Wash the chloroform solution with 10 cc. of water and filter it into a beaker, previously dried and weighed, carefully washing the filter and the stems of the funnels with chloroform. Evaporate it on the water bath; add a few cc. of alcohol, evaporate again, dry at 100° C. for 30 minutes, and weigh. Multiply the weight of the residue in grams by 10 to obtain percentage of total alkaloids.

In addition to the chemical tests here outlined, the sample should be subjected to a microscopic examination by an experienced microanalyst.

The percentage of ash in samples of hellebore prepared from washed or partially washed roots will vary from 3 to 15 per cent, although the ash in ordinary commercial samples may be as high as 25 or 30 per cent. The ash insoluble in hydrochloric acid is an index of the quantity of dirt in the product and in clean samples should not run over 8 per cent, although many commercial samples will contain as high as 20 or 25 per cent. The alkaloids will vary from 0.5 to 3.0 per cent, but will average about 1.0 per cent.

LARKSPUR EXTRACTS

Larkspur extracts are largely used for the control of head lice and usually are prepared from the seeds of *Delphinium consolida*. However, a similar product is prepared from the seeds of *Delphinium staphisagria*, and some of the products on the market are extracts of mixtures of these seeds. The active principles of these extracts are considered to be the alkaloids, of which there are several. As they occur on the market these products contain, in addition to the alkaloids, alcohol, water and frequently acetic acid and glycerine.

Preliminary Determinations.—Note the color and odor of the solution, and determine its specific gravity.

Total Solids.—Evaporate 10 cc. of the sample to dryness in a platinum dish and dry for 2 hours at the temperature of boiling water. Cool and weigh. Calculate and report the residue as percentage of total solids.

Ash.—Ash the residue of total solids at a low red heat, cool, and weigh. Calculate and report as percentage of ash.

Alcohol.—In the absence of acetic acid, pipet a 25 or 50 cc. aliquot (depending on the proportion of alcohol present as shown by the specific gravity of the sample), into a 200 cc. side-neck flask, add about 100 cc. of water, and distil into a 100 cc. volumetric flask until the distillate nearly reaches the mark. Make to volume and determine the specific gravity of the distillate. From the specific gravity calculate the percentage of alcohol from the table.¹

In the presence of acetic acid, add sufficient sodium hydroxide solution to hold the acetic acid, and proceed as just described.

Acidity.—Dilute 10-25 cc. of the sample according to the proportion of acetic acid present and the color of the sample, to about 150 cc. and titrate with 0.2 *N* sodium hydroxide solution, using phenolphthalein as indicator. Calculate and report as percentage of acetic acid.

Glycerol

REAGENTS

(a) *Milk of lime.*—Slake 15 grams of calcium oxide with water and dilute to 100 cc.

(b) *Absolute alcohol-anhydrous ether mixture.*—Mix 2 volumes of absolute alcohol with 3 volumes of anhydrous ether.

DETERMINATION

Evaporate 20-50 cc. of the aqueous solution in a porcelain dish to a volume of about 10 cc. Treat the residue with about 5 grams of fine sand and 4-5 cc. of milk of lime for each gram of total solids present, and evaporate almost to dryness. Treat the moist residue with 50 cc. of alcohol, 90 per cent by volume; remove the substance adhering to the sides of the dish with a spatula; and rub the whole mass to a paste. Heat the mixture on a water bath, with constant stirring, to incipient boiling and decant the liquid through a filter into a small flask. Wash the residue repeatedly by decantation with 10 cc. portions of hot 90 per cent alcohol until the filtrate approximates 150 cc. Evaporate the filtrate to a sirupy consistency in a porcelain dish on a hot, but not boiling, water bath; transfer the residue to a small glass-stoppered, graduated cylinder with 20 cc. of absolute alcohol; and add 3 portions of 10 cc. each of anhydrous ether, shaking thoroughly after each addition. Let stand until clear, pour off through a filter and wash the cylinder and filter with the mixture of absolute alcohol and anhydrous ether, also pouring the wash liquor through the filter. Evaporate the filtrate to a sirupy consistency, dry for an hour at the temperature of boiling water, weigh, ignite, and weigh again. Calculate the percentage loss in weight and report as percentage of glycerol.

¹ *Methods of Analysis, A. O. A. C.*

Total Alkaloids.—Method I

REAGENTS

(a) *Wagner's reagent*.—Dissolve 2 grams of iodine and 6 grams of potassium iodide in a very small quantity of water and dilute to 100 cc.

(b) *Approximately 5 per cent sulfuric acid*.—Pour 29 cc. of concentrated sulfuric acid into several hundred cubic centimeters of water contained in a liter volumetric flask and dilute to the mark.

(c) *Sodium hydroxide solution*.—Dissolve 450 grams of sodium hydroxide in water and dilute to 1 liter.

DETERMINATION

Evaporate a 20–25 cc. portion of the sample in a small dish on a steam bath or in a current of air until all alcohol is expelled. Transfer to a 200 cc. separatory funnel, add an excess of strong sodium hydroxide solution, and extract 3 times with chloroform, using 15 cc. for each extraction. To test the solution for alkaloids, remove several cubic centimeters with a glass tube, acidify with sulfuric acid, and add Wagner's reagent. A dark brown precipitate indicates alkaloids. If this test shows alkaloids to be present, add just sufficient sodium thiosulfate to redissolve the precipitate, return the solution to the separatory funnel, and continue the extraction to completion.

Extract the chloroform solution containing the alkaloids (and impurities) with 5 per cent sulfuric acid, using 10–15 cc. each time, until the extract gives no test with Wagner's reagent. Five extractions are usually sufficient to remove all the alkaloids. Make the acid solution alkaline with excess of sodium hydroxide solution and extract with three 15 cc. portions of chloroform. (If the chloroform solution resulting from the first series of extractions is free from color it is probably unnecessary to further purify it by the sulfuric acid and second chloroform extractions just described.)

Wash the chloroform extracts once with 5–10 cc. of water and then filter into a weighed beaker. Wash the separator and funnel well with chloroform, add to the extract in the beaker, and evaporate to dryness on a steam bath or in a current of air. Add a few cubic centimeters of alcohol and again evaporate to dryness. Continue the drying at 100° C. for 10 minutes, cool, and weigh. The alkaloid residue should be free from color. From this weight calculate the percentage of alkaloids.

Notes on Method I.—It is necessary to remove alcohol if present, otherwise a certain quantity of alkaloids will always be held back in the aqueous liquid. In the analysis of larkspur preparations heat should be avoided as much as possible because the alkaloids are easily decomposed. A large excess of sodium hydroxide is necessary to effect complete liberation of the alkaloids. Ammonia should not be used for this purpose. The first chloroform extract contains various impurities, and the extraction with sulfuric acid separates the alkaloids from this extraneous matter. It is

recommended that the analysis be carried along without interruption after the extractions are begun since decomposition occurs on standing, especially in alkaline solution.

*Method II (Rapp's Method)*¹

REAGENTS

(a) *Sodium sulfate*.—Crystallized salt.

(b) *Plaster of Paris*.

The other reagents are described under Method I.

DETERMINATION

Evaporate a 20 or 25 cc. aliquot of the sample to about 5 cc. and transfer to a 4 ounce wide-mouth bottle; wash out the evaporating dish and add the washings to the solution in the bottle. The volume of sample and washings should not exceed 15 cc.

Add 2 grams of sodium sulfate, then sodium hydroxide in excess, 25 cc. of chloroform, and 15 grams of plaster of Paris; stopper the bottle and shake vigorously for 5 minutes. Add 10 grams more of the plaster of Paris and shake until the chloroform separates from the emulsion. If necessary, continue to add plaster of Paris in 5 gram portions and shake until separation occurs.

Decant and save the chloroform and then wash out the bottle in the following manner: Add 10 cc. of chloroform, shake for 1 minute, decant the chloroform, and add it to the first chloroform extract. Again add 10 cc. of chloroform and 5 grams of plaster of Paris and shake. At this point the mass, which has previously clung to the wall of the bottle, should fall away and form numerous balls. If this does not occur, continue to add plaster of Paris in 5 gram portions with shaking until it does occur.

Continue the addition and decantation of chloroform once or twice more, or until all the alkaloids are removed. From this point proceed as directed in method I, beginning with "Extract the chloroform solution containing the alkaloids and impurities with sulfuric acid."

Notes on Method II.—Method II has a wide range of application. It is especially valuable for the determination of alkaloids in extracts of larkspur that form troublesome emulsions. Its chief virtue is that it effects a separation of immiscible solvents that ordinarily would be difficult or impossible. The plaster of Paris at first forms an emulsion with the chloroform; the emulsion is then broken by the addition of further quantities of this reagent, which holds the water and extraneous matter, while the chloroform takes out the alkaloids.

¹ *Pharm. Ztg.*, 65, 801 (1920).

The original aqueous volume is kept down to 15 cc. in order to avoid the use of excessive quantities of plaster of Paris, and the sodium sulfate retards the setting of this material.

DERRIS

Derris is widely known as a powerful East India fish poison, and it is coming into quite extensive use as an insecticide. McIndoo, Sievers and Abbott¹ tested several species of derris and found the species *Derris elliptica* and *Derris uliginosa* to be very effective against certain types of insects. The powdered roots or the extracts prepared from them act as contact and stomach poisons.

According to present information derris derives its activity mainly from rotenone (sometimes called tubatoxin), which is a white crystalline substance having the empirical formula $C_{23}H_{22}O_6$ and a melting point of 163° C. It also contains other toxic substances, but their toxicity is much less than that of rotenone.

Very little work has been done on the determination of rotenone in derris root. The following method has been suggested by Roark:²

Extract 50-100 grams of root (ground to pass a 20-mesh sieve) with ether for 8 hours in a Soxhlet extractor. Concentrate the extract to about 25 cc. in a 125 cc. beaker-flask. Wash the original container with small portions of ether, using a maximum of 25 cc. Add these washings to the extract and again concentrate to about 25 cc. Stopper the flask with cotton and set the solution aside for a day to allow the rotenone to crystallize. (Crystallization may be hastened by scratching the inside of the vessel. If the extract evaporates to a gummy consistency with no sign of separation of crystals, the addition of a small quantity of ether often aids crystallization.)

Filter through a hardened filter in a weighed Gooch crucible, wash with 10 cc. of ether in small portions, dry the residue at 105° C. for 30 minutes, and weigh as rotenone. If an appreciable quantity of rotenone is present, it will usually separate readily and when washed it is white and of a high degree of purity.

DERRIS PREPARATIONS

At present no satisfactory methods are available for the analysis of commercial preparations containing derris extract. The nearest approximation is to extract the rotenone, resins, and unsaponifiable material by means of ether, evaporate the ether to small volume, and then precipitate the rotenone along with some resin from the other unsaponifiable products by the addition of petroleum ether. The precipitate is filtered off, washed once with petroleum ether, then dried at 105° C., and weighed.

¹ *J. Agr. Research*, **17**, 177 (1919).

² *Malayan Agr. J.*, **18**, 455 (1930).

³ *J. Chem. Soc. Trans.*, **88**, 1367 (1903).

CHAPTER XIV

COAL TAR PRODUCTS

Numerous coal tar products are used as insecticides and disinfectants. The most important, both on the basis of total quantity used and total value, is creosote oil, which is used mainly as a wood preservative and also against chicken mites and certain other insects. Anthracene oils, sometimes referred to as "carbolineums," are used for much the same purposes as creosote oils.

Emulsions made from creosote oils or crude carbolic oils, rosin soap and water, known as coal-tar creosote dips, have been used against some of the parasitic insects of domestic animals. On account of their questionable value as a means of control and because there is danger of injury to the animals, particularly when used with hard water, they are not used for this purpose now as much as formerly.

Kerosene-cresylic acid mixtures have been used as contact insecticides against such household insects as roaches and bed bugs. Naphthalene has long been known as an effective control for moths and, more recently, paradichlorobenzene has come into use for the same purpose. This latter product has also been found to be a very efficient soil fumigant for use against the peach borer, and more than half a million pounds are used annually for this purpose.

Phenol (C_6H_5OH) is one of the very oldest disinfectants and is still used to a large extent. Liquor cresolis compositus and products similar to it, which are often sold as "saponified cresol solutions" or under trade names, have a wide field of application. Some that are made from special types of tar acids are much more powerful as disinfectants than phenol.

Emulsifying coal tar disinfectants also occupy an important place since they can be made cheaply and are used where it would not be practicable to apply a more expensive preparation. Crude carbolic acid is also used to some extent as a disinfectant, but its usefulness is rather limited because it is not miscible with water.

PHENOL

Phenol (C_6H_5OH), commonly called carbolic acid, was originally recovered solely from the "carbolic oil" obtained in the distillation of coal tar, but now it is also manufactured synthetically from benzene. Pure phenol melts at 40.8° and boils at 182.6° C. The U. S. Pharmacopeia

recognizes two phenolic products, the crystallized substance containing not less than 98 per cent of phenol and "liquefied phenol" obtained by adding 10 per cent of water to the crystallized product. The only determinations made on these products are the melting point in the case of the crystallized material and the phenol content in the case of liquefied phenol.

Melting (Congealing) Point.—Determine as directed on p. 483. The observed temperature should not be below 39° C.

Phenol Content.—Applicable to phenol or liquefied phenol.

REAGENTS

(a) *0.1 N bromate solution.*—Dissolve 3 grams of potassium bromate and 50 grams of potassium bromide in water, dilute to 1 liter, and standardize against the 0.1 *N* thiosulfate solution as follows: Transfer a 30-40 cc. aliquot to a glass-stoppered flask and add 5 cc. of hydrochloric potassium iodide solution. From this point proceed as described under "Determination."

(b) *0.1 N thiosulfate solution.*—Prepare as directed on p. 535.

(c) *Potassium iodide solution.*—Dissolve 20 grams of potassium iodide in water and dilute to 100 cc.

DETERMINATION

Dissolve about 1.5 gram of sample, accurately weighed, in sufficient distilled water to make 1000 cc. Transfer an aliquot portion of this solution, containing from 0.038 to 0.041 gram of phenol, to a 500 cc. glass-stoppered flask having a long narrow neck, add 30 cc. of 0.1 *N* bromate solution and 5 cc. of hydrochloric acid, and immediately insert the stopper. Shake the flask repeatedly during 30 minutes, allow it to stand for 15 minutes, remove the stopper just sufficiently to introduce quickly 5 cc. of the potassium iodide solution, being careful that no bromine vapor escapes, and immediately stopper the flask. Shake the latter thoroughly, remove the stopper, and rinse it and the neck of the flask with a little distilled water, so that the washings may flow into the flask; then add 1 cc. of chloroform, shake the mixture well, and titrate with 0.1 *N* sodium thiosulfate, using starch as an indicator. Each cubic centimeter of 0.1 *N* bromate solution corresponds to 0.001568 gram of C_6H_5OH .

Phenol in the Presence of Other Tar Acids.—The method of determining phenol by bromination is not applicable in the presence of cresol or other higher homologs of phenol, because they also absorb bromine. The cresols are said¹ to absorb two atoms of bromine in the cold, and on this basis a method has been worked out for determining phenol and cresols in mixtures. However, when phenol is present with other coal tar acids, their nature is usually unknown and therefore the method is not

¹ Jarvinen, *Z. anal. Chem.*, **71**, 108 (1927).

generally applicable. Since the passage of the Federal caustic poison act, it has been necessary to determine the actual phenol (C_6H_5OH) in such mixtures. Chapin¹ has suggested a colorimetric method based on the color formed with Millon's reagent. This has been found to be applicable to such products as cresol, liquor cresolis compositus, saponified cresol solution, emulsified coal tar disinfectants, crude carbolic acid and kerosene phenol solutions. The principal interfering substance is methyl salicylate, which is very frequently a constituent of the commercial kerosene phenol insecticides. The method follows.

REAGENTS

(a) *Dilute nitric acid*.—Blow air through strong nitric acid until it is colorless, then dilute 1 volume of this acid with 4 volumes of water.

(b) *Millon's reagent**.—Treat 2 cc. of mercury in a 200 cc. Erlenmeyer flask with 20 cc. of strong nitric acid. Place the flask under a hood and after the first violent reaction is over, shake as much as necessary to effect subdivision of the mercury and maintain action. After about 10 minutes, when the action has practically ceased, even in the presence of undissolved mercury, add 35 cc. of water. If basic salt separates, add sufficient dilute nitric acid to dissolve it. Next add a 10 per cent solution of sodium hydroxide dropwise with thorough mixing until the curdy precipitate following a single drop no longer redissolves but disperses to an evidently permanent turbidity. Then add 5 cc. of dilute nitric acid and mix well. The solution deteriorates and should not be used later than the day following the day of preparation.

* (Millon solution is dangerously poisonous and should not be transferred with an ordinary pipet and mouth suction unless a protective trap of some kind is used).

Standard phenol.—Prepare a stock solution by dissolving a weighed quantity of the pure substance possessing a congealing point of not lower than 40° C., in a sufficient quantity of water to make not less than a 1 per cent solution. From this stock solution make a 0.025 per cent solution of phenol in distilled water. This second solution constitutes the final standard, and it should be prepared on the day of use.

Dilute formaldehyde solution.—Dilute 2 cc. of the commercial 37 per cent solution to 100 cc. with distilled water.

APPARATUS

Nessler cylinders.—50 cc. tall form, matched.

Test tubes.—About 180 by 20 mm. provided with rubber stoppers and marked at 25 cc. A file scratch will serve to mark the test tubes.

Bath.—For heating the test tubes. This may be extemporized from a beaker containing a disk of wire gauze raised somewhat from the bottom.

DETERMINATION

Weigh by difference about 2.5 grams of commercial cresol or 5 grams of a saponified cresol preparation into a 250 cc. volumetric flask and make to the mark with

¹ U. S. Dept. Agr. Bull. 1308.

water. (In products consisting largely of kerosene the latter will form a separate layer. This layer has been found to retain very little phenol, and it is preferable to bring the water level to the mark on the flask and take aliquots from the aqueous portion only.)

Transfer a 5 cc. aliquot of the solution to a 200 cc. volumetric flask shortly before the determination is to be carried out, dilute to about 50 cc., add one drop of methyl orange indicator and then dilute nitric acid until the solution is practically neutral, make to the mark and mix well. In the case of saponified cresol solutions, use about 5 grams and dilute in a similar manner.

Place 5 cc. of the diluted solution in each of two of the graduated test tubes, and in each of two additional test tubes place 5 cc. of the standard phenol solution. Next flow 5 cc. of the Millon reagent down the side of each tube, mix, and place the tubes in a bath of boiling water; continue the boiling for exactly 30 minutes; cool immediately and thoroughly by immersion in a bath of cold water for at least 10 minutes, and then add 5 cc. of the dilute nitric acid to each tube.

After brief mixing add 3 cc. of the dilute formaldehyde to one of each pair of tubes, adjust the contents of each tube to the 25 cc. mark with water, stopper, shake well, and then put aside to stand overnight. The next day the tubes to which formaldehyde has been added will have faded to a yellow, while the others will show an orange or red tint.

Pipet 20 cc. from each of the two phenol tubes and transfer to 100 cc. volumetric flasks, treat each with 5 cc. of the dilute nitric acid, make to the mark, and mix. The red flask contains the "phenol standard," and the yellow flask the "phenol blank." Transfer these phenol solutions to burets. Pipet 10 cc. of each sample solution into Nessler tubes. The orange constitutes the "unknown" and the yellow the "sample blank," and each Nessler tube must be distinctly marked to avoid confusion. Next add to the "sample blank" a measured quantity of "phenol standard" from its buret and add the same volume of "phenol blank" to the unknown; thoroughly agitate, aided by the insertion of rubber stoppers if necessary, and compare the colors. When the tubes have been brought directly to a match calculate the percentage of phenol on the basis that each cubic centimeter of the phenol standard employed is equivalent to 1 per cent if a 5 gram sample was used.

Chapin mentions the following precautions.—A pair of phenol tubes affords sufficient final solutions for assaying several unknowns, but all the latter must have accompanied the phenol solutions throughout the entire process with identical reagents and treatment. If the end point has been inadvertently overrun it is possible to work back to it; but, since mistakes are easy to make in this procedure, it is better to repeat the comparison on fresh portions from the original tubes. Too much delay in matching the tubes must be avoided once the titration has been started since the excess of formaldehyde yet present in the blanks may have time after mixture to affect the intensity of the red color.

It may be noted that the quantity of the phenols entering a single test, about 1.25 mg., is much less than the 4 mg. recommended in the original

paper. It was then shown that the method gave distinctly low results, supposedly owing to the effect of formaldehyde. Later investigations have indicated the low results to be, in fact, primarily due to the adsorption of higher homologs of phenol. As the concentration of the total phenols in the sample is reduced, these precipitates become of less significance and the results for phenol approach the theoretical.

Phenol in Presence of Other Tar Acids and Salicylates.—In speaking of the method for the estimation of phenol just described Chapin¹ says that salicylic acid and beta-naphthol obviously invalidate the test. Methyl salicylate will be present in some products, such as fly sprays, in which it is desired to estimate phenol. If the phenol is determined by the previous method, the results will very likely be high. However, the following methods have been found capable of satisfactorily separating the salicylate previous to the estimation of phenol.

Kerosene method.—The reagents and apparatus are described under the preceding method. To 10 cc. of the sample add 50 cc. of kerosene, and extract with three successive portions of water. Combine the aqueous extracts and filter them through a wet filter into a 500 cc. volumetric flask. Make to volume, mix, and proceed by the method described on p. 585, beginning with "Transfer a 5 cc. aliquot of the solution to a 200 cc. volumetric flask."

Saponification method.—Use reagents and apparatus described under the preceding method.

DETERMINATION

To a weighed sample of approximately 20 grams contained in an Erlenmeyer flask equipped with an air condenser add 30 cc. of 95 per cent ethyl alcohol and a few grams of potassium hydroxide. Heat on the steam bath for 1-2 hours to saponify the methyl salicylate. Transfer to a beaker and continue heating on the steam bath until the alcohol is completely expelled. Add water and extract three times with ether. Reject these ether extracts, acidify the aqueous layer with sulfuric acid to liberate the phenols, and again extract three times with ether. Combine the ether extracts and extract them twice with a saturated aqueous solution of sodium bicarbonate and twice with water. The bicarbonate combines with and removes the salicylic acid, but does not affect the phenol, which is left with the ether. Evaporate the ether to small bulk (it is not necessary to remove all the ether) and transfer the residue to a liter volumetric flask. Fill the flask to the mark with water, mix the contents, and determine the phenol by the preceding method, beginning with "Transfer a 5 cc. aliquot of the solution to a 200 cc. volumetric flask * * * ."

¹ *J. Ind. Eng. Chem.*, **12**, 771 (1920).

LIQUOR CRESOLIS COMPOSITUS

Liquor Cresolis Compositus, or *Compound Solution of Cresol*, is a Pharmacopeia product made from cresol, linseed oil soap and water. It is one of the most common disinfectants used in hospitals, around dwellings in cases of infectious diseases, and as a general disinfectant. It is more effective as a disinfectant than phenol and is miscible with water in all proportions.

Cresol¹**REAGENTS**

(a) *Kerosene*.—Extract commercial kerosene with one-tenth its volume of 15 per cent sodium hydroxide solution, and wash with water until free from alkali.

(b) *Sodium hydroxide solution*.—Dissolve 15 grams of sodium hydroxide in water and dilute to 100 cc.

(c) *Sulfuric acid*.—Make a mixture of 27 cc. of concentrated sulfuric acid and 46 cc. of water. Determine the strength of this solution, and if it does not fall between 49 and 51 per cent H_2SO_4 , adjust it.

(d) *Anhydrous copper sulfate*.—Heat crystallized copper sulfate in a muffle until it is of a uniform light gray tint.

APPARATUS

(a) *Distilling bulb*.—Use a 200 cc. distilling flask having at approximately the center of the neck an outlet tube inclined at an angle of from 70° to 75° with the lower portion of the neck. The length of the neck should be from 10 to 12 cm. and its inside diameter from 18 to 24 mm. The length of the outlet tube should be from 10 to 12 cm. and its inside diameter from 5 to 6 mm.

(b) *Condenser*.—Use a straight glass condenser having a water jacket 40-60 cm. in length, the distance from the upper end of the water jacket to the neck of the bulb being from 18 to 25 cm.

(c) *Thermometer*.—Preferably an accurately standardized thermometer of the Anschütz type.

(d) *Asbestos board*.—A piece of asbestos board 12-15 cm. square and from 3 to 5 mm. in thickness, having a circular hole 25 mm. in diameter in its center for the reception of the bulb. The edge of the asbestos around the hole should fit closely to the bulb when the latter is set into it.

DETERMINATION

Mix in a 500 cc. distilling flask 50 cc. of compound solution of cresol, accurately measured at $25^\circ C.$, with 150 cc. of kerosene that has been shaken with about one-tenth its volume of 15 per cent sodium hydroxide solution and then washed with water until free from alkali. Add 3 grams of sodium bicarbonate and distil through an upright condenser at the rate of not more than two drops per second,

¹ U. S. Pharmacopeia X Method slightly modified.

until the distillate comes over strongly yellow, receiving the distillate in a 250-300 cc. separatory funnel. Discard the lower aqueous layer, shake the kerosene layer with 10 cc. of the 50 per cent sulfuric acid and allow to stand for 2 hours; then draw off the acid layer completely and discard it. Add to the kerosene layer 40 cc. of the sodium hydroxide solution, accurately measured at 25° C., and shake well for 5 minutes; then allow to stand until complete separation has taken place, and draw off the sodium hydroxide layer into a graduated cylinder. Shake the kerosene layer again with a fresh portion of 20 cc. of the sodium hydroxide, accurately measured at 25° C.; allow the two layers to separate completely; and again draw off the sodium hydroxide layer into the graduated cylinder. Adjust the sodium hydroxide solution in the graduated cylinder to a temperature of 25° C. and note the volume. The difference between the volume noted and the total volume of sodium hydroxide solution used represents the volume of cresol present in 50 cc. of compound solution of cresol. This difference for a U. S. P. product should be not less than 23 cc. and not more than 26 cc.

Transfer the sodium hydroxide solution of the cresol obtained as above to a separatory funnel and add sufficient hydrochloric acid to render the solution distinctly acid. Allow the cresol to separate completely and draw off the lower aqueous layer. Wash the cresol with several successive portions of 20 cc. each of a saturated aqueous solution of sodium chloride until the washings are neutral or only slightly acid; then add to the washed cresol about 5 grams of the freshly dehydrated copper sulfate, shake gently at frequent intervals during 3 hours, and allow to stand overnight. The cresol decanted from the copper sulfate should meet the distillation requirements for cresol when determined by the following method.¹

Place the distilling bulb described under apparatus in an upright position in the perforation in the asbestos board and connect it with the condenser. The outlet tube is to extend from 25 to 35 mm. into the condenser beyond the connecting stopper.

Measure the recovered cresol to be tested, note the temperature of the liquid and transfer it as completely as possible to the distilling bulb. Use the same cylinder as the receiver for the distillate without rinsing out any of the adhering liquid. Insert the thermometer through a stopper so that its lower end is 2-3.5 cm below the center of the orifice of the outlet tube and heat with a Bunsen burner protected from drafts until the liquid begins to boil; then distil at the rate of 4-5 cc. per minute, collecting the portion which comes over between 195° and 205° in the same cylinder which was used in measuring the cresol. Bring the distillate to the same temperature at which the cresol was originally measured and note the volume. It should be at least 90 per cent of the original.

This method for total cresols is easy to carry out and quite accurate when applied to a product containing U. S. P. cresol. However, in the assay of preparations in which a considerable portion of the lower boiling phenols is present low results are obtained, due apparently to solution of phenols in the aqueous layer from the original distillation. To correct for this the aqueous layer and the acid wash water should be combined

¹ U. S. Pharmacopeia X. 433.

and extracted with ether. The phenols recovered in this way, amounting to from 1 to 2 cc., indicate an error in the method when applied to such preparations of from 2 to 4 per cent.

U. S. P. compound solution of cresol should be made from U. S. P. cresol, but coal tar acids distilling somewhat higher or lower than cresol may be purchased at much lower prices than cresol, and they are sometimes used as substitutes for it. Soluble disinfectants made from such tar acids have properties quite similar to those of compound solution of cresol and are generally even more effective as disinfectants. Under such conditions there is considerable tendency to put an adulterated article on the market which, of course, constitutes unjust competition for the honest manufacturer. It is for this reason that the distillation test has been added to the Pharmacopœia assay. In the method here suggested 5 grams of dehydrated copper sulfate has been substituted as the drying agent for the cresol in place of the 5 grams of ignited potassium carbonate recommended by the Pharmacopœia, since Griffin¹ has shown that the potassium carbonate reacts to some extent with the cresol and therefore is not a satisfactory drying agent. The dehydrated copper sulfate has been found fairly satisfactory for the purpose even though it does not remove the last traces of water.

After the cresol has been dried the mixture of cresol and copper sulfate may be centrifugalized before the cresol is poured off. This will usually result in a somewhat better yield. In practice it has been found that about 18 cc. of cresol will be recovered from each determination. This is a rather small quantity to distil in a 200 cc. distillation bulb, and a 25 cc. or 50 cc. bulb would seem to be preferable. However, since the former is prescribed by the Pharmacopœia it must be used. Actual tests have shown that a true cresol can be satisfactorily identified by this method.

The following procedure gives good results in the complete analysis of liquor cresolis compositus.

Water.—Determine water in a 50 gram sample by distilling with xylene into a Dean and Stark type distilling tube receiver as directed for water in soap, p. 561.

Unsaponified Material.—Weigh about 20 grams of sample into a 125 cc. Squibb separatory funnel, add about 40 cc. of ether and 40 cc. of water, and shake the mixture. Let it stand until it has separated into layers and draw off the aqueous layer into a second funnel. Add 40 cc. of ether to the aqueous portion in the second separatory funnel, shake the mixture, let it stand until separated, and draw off the aqueous layer into a third funnel. Repeat the washing of the aqueous layer

¹ *J. Am. Pharm. Assoc.*, 15, 196 (1926).

with another 40 cc. of ether in the third funnel. Draw off and reserve the aqueous layer. Successively wash the ether fractions in the three separatory funnels, first with 40 cc. of 10 per cent sodium hydroxide solution, then with 25 cc. of 10 per cent sodium hydroxide solution and finally with 25 cc. of water. Combine the ether fractions in a tared 250 cc. beaker and carefully distil off the ether on a water bath. (The last of the ether may be evaporated with a current of air at room temperature.) Weigh the residue and from this weight calculate the percentage of unsaponified material. It will include both the unsaponified matter from the linseed oil and any neutral oils in the cresol.

Fatty Acids.—Combine the alkaline and water extracts from the determination of the unsaponified material and transfer to a 500 cc. Kjeldahl flask. Acidify with dilute sulfuric acid (1 + 4) and steam distil until a test portion of the distillate shows no coloration with ferric chloride solution. Usually all the phenols will come over in 400 cc. of distillate. Cool the residue in the flask and extract it with three 40 cc. portions of ether, wash the ether once with water, combine the ether extracts in a tared 250 cc. beaker, evaporate the ether on a water bath, and weigh the residue. From this weight calculate the percentage of fatty acids. To convert the percentage of fatty acids to fatty anhydrides, multiply by the factor 0.97.

Iodine Number of Fatty Acids.—The formula for liquor cresolis compositus calls for linseed oil and in the assay of this product it is necessary to identify the fatty acids obtained from it. This may most readily be done by determining their iodine number. Either the Hanus method¹ or the Wijs method² may be used. The Pharmacopeia states that linseed oil should have an iodine number not less than 170. Holde³ gives the iodine number of the fatty acids from linseed oil as 179–182. It is possible that if the fatty acids have been heated too long and become oxidized the results obtained may be a little lower.

Phenols (Cresol).—Determine phenols by the modified U. S. Pharmacopeia method, p. 588, or by the following method:

Transfer the steam distillate containing the phenols, which was obtained in the determination of fatty acids, to a separatory funnel; saturate with salt; and extract three times with ether, using about 50 cc. each time. Combine the ether extracts in a separatory funnel and extract them successively with 15 and 10 cc. of 25 per cent sodium hydroxide solution and 10 cc. of water. Retain the ether. Combine the aqueous extracts, heat them on the water bath until all the ether has been evaporated, cool, and acidify with dilute sulfuric acid (1 + 3). Transfer the mixture to a buret, let stand for an hour for the phenols to separate, and then read the volume of phenols which have separated. Determine the water on a portion of about 5 cc. of the phenols by distillation with xylene as in the determination of water in liquor cresolis compositus and subtract the calculated volume of water from the measured volume of phenols. Run the aqueous layer from under the phenols into the ether, which has already been used for extraction of the distillate and retained. Shake the mixture well, separate the ether, and evaporate it on the water bath, being careful not to lose any phenols. Calculate the total weight of phenols in the product by multiplying the corrected volume by the factor 1.05 and adding to it that which

¹ *Methods of Analysis, A. O. A. C.*

² *Examination of Hydrocarbon Oils.* John Wiley & Sons, New York, 1915.

has been recovered after evaporating the ether. This method, while somewhat complicated, has been found to give satisfactory results in the hands of an experienced analyst.

Sodium and Potassium Oxide.—Determine by the method described under soap on p. 561.

Glycerol.—Determine glycerol by a modification of the method described for glycerol in soap on p. 562. A 50 gram sample of liquor cresolis compositus should be used and after decomposing with sulfuric acid it is necessary to extract the fatty acids and phenols with ether. Then proceed as with the acid water from which the fatty cake has been removed.

A method that is more rapid than that already described but which may give somewhat less accurate results is based on the method for glycerol in wines by direct weighing.¹ The procedure follows.

Dissolve a 20 gram sample of the liquor cresolis compositus in 50 cc. of water and add the volume of normal sulfuric acid solution which will be just sufficient to neutralize the total alkali in the sample. Extract the mixture three times with ether, washing the ether each time with water. Combine the aqueous portions and evaporate on the steam bath to a sirupy consistency. Take up with absolute alcohol, warm, and filter from sodium sulfate. Repeat the evaporation and extraction with absolute alcohol. Evaporate the alcohol, and, if the residue shows traces of tarry material, wash once with 5 cc. of anhydrous ether. Evaporate traces of ether, dry for an hour at the temperature of boiling water, and weigh. Ignite the residue, weigh, and regard the loss of weight as glycerol.

SAPONIFIED CRESOL SOLUTIONS

It has been found that products of the type of liquor cresolis compositus, which are made from coal tar acids other than cresol and soaps other than linseed oil soap, are satisfactory for many disinfecting purposes. In fact, some of them are much more effective than liquor cresolis compositus for certain purposes. As a result a large number of these preparations are sold under the name of "Saponified Cresol Solution" or under proprietary names.

The methods of analysis described under "Liquor Cresolis Compositus" are applicable to saponified cresol solutions. In addition, certain other tests are at times necessary.

Chill Test.—It has been found that two difficulties may be encountered in the use of saponified cresol solutions. If a proper soap is not used or if the propor-

¹ *Methods of Analysis, A. O. A. C.*

tions are not right, separation or solidification may occur, particularly at low temperatures. To detect this fault Chapin¹ has suggested a chill test as follows:

Half fill a 180 by 20 mm. test tube with the sample, stopper, and immerse it at least three-fourths in a bath held at 0° C. for 3 hours. The contents of the tube immediately after withdrawal from the bath should flow when the tube is tilted and should show no separation of soap, either in mass or as a pronounced turbidity.

Solution-Rate Test.—If too large a proportion of high-boiling coal tar acids is used in the preparation of a saponified cresol solution it will not be readily miscible with water in all proportions. In the higher concentrations it will form a gelatinous, almost solid mass. In the lower concentration it will be very slow to go into solution. An empirical test of speed of solution has been proposed by Chapin. A description of the method follows.

APPARATUS

(a) *Measuring cylinder.*—Ordinary 250 cc. glass-stoppered, graduated type, about 35 cm. in height and holding 300 cc. to the neck.

(b) *A marble*—12–14 mm. in diameter.

DETERMINATION

Fill the cylinder nearly to the neck with distilled water at 25° C., drop in the marble, and rapidly pour in from a graduate 10 cc. of the sample, being careful that the liquid does not contain froth or touch the sides of the large cylinder when it is poured. Quickly fill the cylinder to overflowing with distilled water at the same temperature and insert the stopper without trapping any air. Before the sample has fallen to the bottom and formed a layer hold the cylinder vertically between the hands and invert rapidly every 2½ seconds—that is, bring it through a complete cycle of positions in 5 seconds. At the expiration of 2 minutes from the first contact the mixture should be entirely free from globules and jelly particles and not more than faintly opalescent.

CREOSOTE OILS

The term cresote, properly applied, refers to the phenoloid bodies obtained from wood tar, and this is its meaning as used in the U. S. Pharmacopeia. It is used also to refer to a mixture of tar acids obtained from coal tar. The coal tar or wood tar oils from which the creosote (that is, the tar acids) may be extracted with sodium hydroxide are called creosote oils. At the present time, unless specifically stated to the contrary, the term "creosote oil" is understood to refer to the product distilled from a high temperature coal tar such as ordinary coke-oven or gas tar. Common usage in the wood preserving industry has led to a rather general disuse of the word "oil" so that "creosote oil" is usually referred to as "creosote." The American Wood Preservers Association has defined the word "creo-

¹ *Loc. cit.*

sote" as follows: "Creosote in the scientific sense, may be properly defined as any and all distillate oils boiling between 200° and 400° C., which are obtained by distillation from tars consisting principally of compounds belonging to the aromatic series, and containing well defined amounts of phenoloids."

Creosote oils are used in large quantities as wood preservatives and as flotation oils to aid in separating certain ores, particularly the sulfides, from the gangue with which they are mixed. They are also used in the preparation of emulsifiable disinfectants, as insecticides, and in shingle stains and bituminous paints. In the past they have been used in the preparation of some of the animal dips, but more recently it has been found that other dips are better suited than the creosote preparations. In 1927 domestic production of creosote oil was 76 million gallons, and imports for the same year were 96 million gallons.

In testing a creosote oil it is usual to determine water, free carbon (or benzene-insoluble material), tar acids, specific gravity, distillation range and unsulfonated residue.

Water.—Determine water on a 100 cc. sample by distillation into a Dean and Stark type receiver as described on p. 561, or, if the water will separate readily, calculate the percentage from the quantity found in the portion that comes over below 210° C. in the determination of distillation range.

Free Carbon (Benzene-Insoluble Material)

APPARATUS

Extraction apparatus.—A special flask 24 cm. high and 6.5 cm. diameter at the bottom, with a condenser inserted in the top and a filter cup to contain the oil suspended below the condenser (see Fig. 7).

Filter cup.—The filter cup may consist of two thicknesses of hardened filter paper arranged in a cup shape about 1 inch in diameter by $2\frac{1}{2}$ inches long by folding symmetrically, or an alundum crucible may be used. A cap should be furnished for the filter cup. If filter papers are used, they should be soaked in benzene to remove any grease, dried, and kept in a desiccator until ready for use.

DETERMINATION

Weigh 10 grams of the dry oil and transfer it to a weighed filter cup by means of 50 cc. of pure benzene. Add sufficient benzene to the apparatus for use in the extraction, place the filter cup in its support, heat with an electric heater or over the steam bath, and continue the extraction until the descending solvent is practically colorless. Then remove the filter cup, heat it in a steam oven until the solvent is evaporated, cool in a desiccator, and weigh.

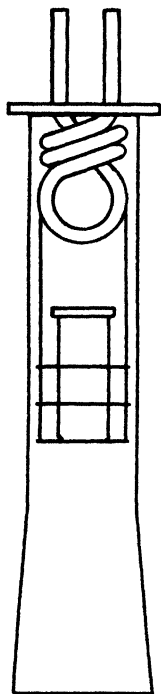


FIG. 7.—Apparatus for Determination of Free Carbon.

Tar Acids.—*Contraction Method.*—No method for the determination of tar acids is entirely satisfactory, but the contraction method described by Weiss¹ is quite generally used.

APPARATUS

Tar acid separatory funnels, type 1 and type 2 (see Fig. 8), and distillation apparatus.

DETERMINATION

Place 100 cc. of the creosote oil in a side-neck distillation bulb fitted with a condenser and thermometer reading to 400° C. and distil until 95 cc. of distillate has come over or until the vapor temperature has reached 400° C. Transfer the distillate to a type 1 tar-acid separatory funnel if it has more than 25 per cent of acids or to a type 2 funnel if it has less than this proportion. Bring the funnel with the oil to constant temperature in a water bath at 60° C. and note the volume of oil. Extract with successive portions of 50 cc. each of 10 per cent caustic soda

¹ *J. Ind. Eng. Chem.*, **10**, 913 (1918).

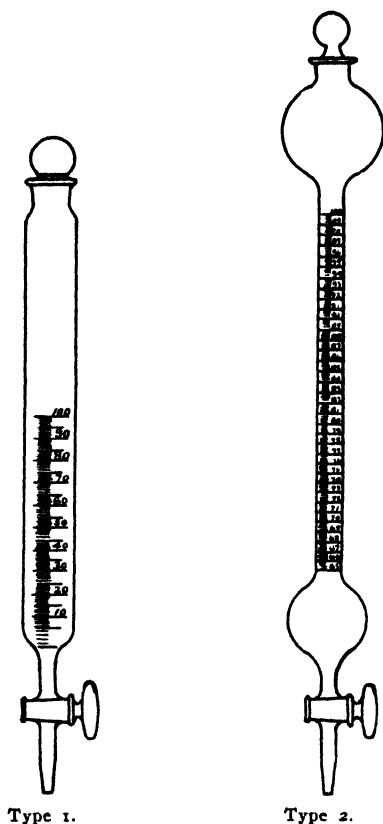


FIG. 8.—Tar Acid Separatory Funnels.

solution, until no further diminution in volume occurs. (In each case the caustic soda solution is added to the funnel, the mixture shaken and allowed to separate at 60° C., the soda solution drawn off, and the volume of the residual oil noted.) When no further contraction in the volume of the oil occurs consider the total diminution in its volume to be tar acids. Since 100 cc. of sample was taken, the number of cubic centimeters shrinkage represents directly the percentage of tar acids by volume.

Hill² states that Weiss has changed this method somewhat and extracts with three 100 cc. portions of 10 per cent sodium hydroxide solution. Also if the oil contains over 35 per cent of tar acids he dilutes it with 1 or 3 volumes of kerosene before making the extraction so as to bring it within

² *J. Ind. Eng. Chem.*, **15**, 799 (1923).

this limit. The result is, of course, multiplied by 2 or 4 as the case may be.

Weiss¹ states that this method gives results which are slightly higher than the true acid content of the oil because the soda dissolves compounds other than phenolic bodies and withdraws them from the oil. In spite of this he considers it the most satisfactory method for general use.

Liberation method.—Weiss also describes a liberation method for tar acids which gives approximately the quantity of tar acids that can be recovered from an oil in practice. Results by this method are usually about 90 per cent of those by the contraction method.

APPARATUS

Use same apparatus as in the contraction method.

DETERMINATION

Distil 100 cc. of the creosote oil as already described. (If the tar acid content is very low, 200 cc. of creosote oil may be distilled so that the results will be more accurate.) Shake the oil in a separatory funnel with successive 25 cc. portions of 15–20 per cent caustic soda solution until no more tar acids are removed. After shaking let the alkaline solution thoroughly settle each time and then draw it off into a beaker. Acidify the combined alkaline extracts with 40 per cent sulfuric acid, taking care to keep the mixture cool at all times. If the tar acid content of the oil is over 5 per cent, measure 65 cc. of a high boiling naphtha into a type 2 tar acid funnel and note the volume. Then pour into it the liberated tar acids and sodium sulfate solution, draw off the aqueous layer and rinse the beaker with it, and again pour it into the funnel. Repeat this rinsing several times so that the phenols will be thoroughly extracted by the naphtha. Allow the funnel to stand until the layers separate perfectly and draw off the sulfate solution. The increase in volume of the naphtha layer is considered to be due to tar acids. If the oil contains less than 5 per cent of tar acids, follow the same procedure but use a separatory funnel that will measure a much smaller volume of naphtha and only 10 cc. of the naphtha to extract the tar acids.

Direct Determination.—Tar acids may also be determined by direct weighing or by direct measuring. In this case correction must be made for the water contained in the tar acids and for the tar acids dissolved in the aqueous solution.

DETERMINATION

Distil the creosote oil and extract with successive 25 cc. portions of 20 per cent sodium hydroxide solution as in the liberation method just described. Successively wash the alkaline extracts with two 25 cc. portions of ether, then combine the alka-

¹ *Loc. cit.*

line extracts in a beaker, heat them on a water bath for a few minutes to expel the ether, cool, and acidify with dilute sulfuric acid (1 + 3), taking care to keep the solution cool during the addition of the acid. If only a small portion of tar acids is present, extract the acidified mixture three times with ether, carefully evaporate the ether on the steam bath, using a gentle air current to remove the last portions, and weigh the tar acids. If a considerable quantity of tar acids is present, transfer the acidified mixture to a 100 cc. buret, drawing some of the solution from the buret to rinse the beaker and returning it to the buret. Let it stand until the tar acids have separated as much as possible and note their volume. Determine the water in a measured portion of the phenols by the xylene distillation method, p. 561. Draw off the aqueous layer and extract it three times with 40 cc. portions of ether, carefully evaporate the ether, and weigh the residual tar acids. Calculate the weight in grams of the measured tar acids by multiplying the number of cubic centimeters by the factor 1.05 (an arbitrary value for the density of the tar acids). To this add the weight of tar acids extracted from the aqueous layer and subtract the weight of water found in the tar acid layer.

Thus if a = measured volume of tar acids in cc.,

b = weight of tar acids in grams extracted from the aqueous layer, and

c = weight of water in tar acids in grams,

Then total weight of tar acids = $1.05 a + b - c$

Although this method appears to be somewhat complicated it has been found to be rather easy of manipulation and gives excellent results in the hands of an experienced worker.

Specific Gravity.—Determine the specific gravity of creosote oil either by means of a hydrometer or a Westphal balance. Since many creosote oils will separate solid material at ordinary room temperature make the determination at 38° C. and compare with water at 15.5° C.

Distillation Range

APPARATUS

A special distillation flask with a capacity of 250–290 cc., an asbestos shield for the flask, an air condenser, and a thermometer as shown in Fig. 9.

DETERMINATION

Weigh 100 grams of the oil into the retort, assemble the apparatus as shown in the figure, and distil at such a rate that at least one drop and not more than two drops per second are collected in the receiver. Change receivers at 210°, 235°, 270°, 315° and 355° C. and weigh the various fractions.

Sulfonation.—At times creosote oils have been adulterated with mineral oil. As an aid in detecting this form of adulteration, the unsulfonated residue is determined. The method used is the same as that described for mineral oil on p. 566. In considering the values obtained it should be borne in mind that a true coal tar creosote oil may show a small proportion of unsulfonated material, the proportion depending to some extent on the method of producing the coal tar from which the creosote oil was made.

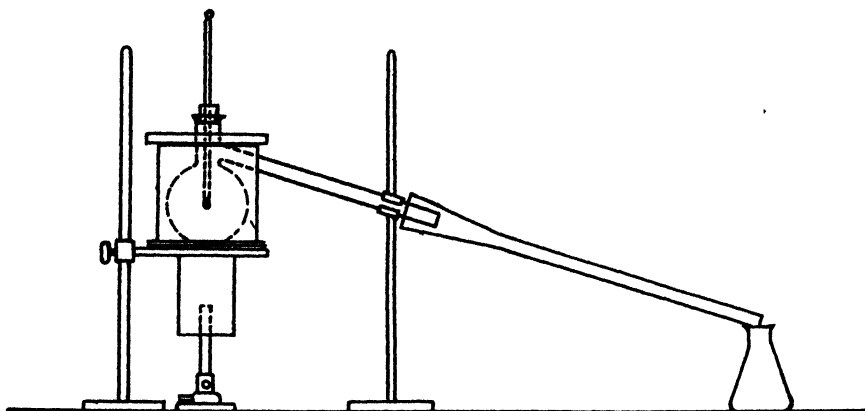


FIG. 9.—Distillation Apparatus.

ANTHRACENE OIL

Anthracene oil is generally defined as the fraction of coal tar that distills above 270° C. It contains the anthracene together with other hydrocarbons and some phenoloid bodies. The anthracene may be recovered from the product and the residual oil used as a wood preservative either mixed with creosote oil or alone. Because this oil is less volatile than the usual creosote oil it has been found valuable for use where only a brush coating is to be given to the wood. The more volatile creosote oils are not so satisfactory for this purpose. Owing to their low volatility the oils from which the anthracene has been recovered have also been found useful for painting poultry houses to kill chicken mites. Many proprietary preparations of this material have been put on the market as "carbolineums."

The methods of analysis for the anthracene oils are exactly the same as the methods already given for creosote oils.

KEROSENE-CRESYLIC ACID MIXTURES

Mixtures of kerosene with coal tar acids are often used for spraying to control certain household insects and to some extent on animals.

Phenols.—If the coal tar acid used is phenol (C_6H_5OH), it is determined by the colorimetric method of Chapin described on p. 585. If the higher tar acids such as cresylic acid are present, the methods described for tar-acids in creosote oil should be used.

Sulfonation.—As a check on the amount of kerosene present the unsulfonated residue is determined by the method described for mineral oil on p. 566. Samples of kerosene tested by this method have given an unsulfonated residue of about 80 per cent. Of course, this cannot be taken as applying to all kerosenes since such products vary considerably in composition. Sulfonation, however, has been found a valuable check in determining the composition of kerosene-cresylic acid preparations.

Specific Gravity.—The specific gravity of the preparation may be determined with either a hydrometer or a Westphal balance. It furnishes another indication of the composition of the product since the specific gravity ($20^{\circ}/4^{\circ}$) of kerosene is usually about 0.80, while that of cresylic acid is about 1.05 under the same conditions.

EMULSIFYING DISINFECTANTS

Emulsifying disinfectants, sometimes called coal tar creosote dips, consist of coal tar acid oils (crude carbolic oils), rosin or fatty soaps, and water. They are black or brown, oily appearing liquids which, when poured into water, form white, reddish or brown emulsions. They are used in large quantities where a cheap disinfectant is desired and are also of value against some of the insects that infest animals. They were formerly widely recommended as dips, but they were found to be rather unsatisfactory for this purpose owing to difficulty in keeping the dipping bath in a condition to assure an effective action and because of the danger of injury to the animals.

The disinfecting value of these preparations depends on the quantity and type of coal tar acids which they contain, on the coal tar oils present, and on the completeness with which the product emulsifies. Those which are made from special types of oils, such as blast furnace tar oils, have high phenol coefficients; others, which have been adulterated with mineral oil or which contain low-grade oils and are not well emulsified, are almost valueless. The products are usually tested bacteriologically to determine their value as disinfectants, but a chemical analysis is also quite commonly required. The methods for the determination of soap and water are fairly satisfactory, but while several methods have been suggested for the neutral oils and phenols none of them is entirely satisfactory. However, they give considerable information as to the composition of the product. The following methods have been used for these determinations.

Water.—Determine water on a 50 gram sample by distilling with xylene into a Dean and Stark type distilling tube receiver in exactly the same manner as described for water in soap on p. 561.

Phenols, Neutral Oils and Fatty or Rosin Acids.—Weigh approximately 20 grams of sample into a 125 cc. Squibb funnel. Add about 40 cc. of ether and 40 cc.

of water and shake the mixture. If the mixture does not separate into two layers on standing, add a little 25 per cent sodium hydroxide solution and shake again. It will then usually separate into layers. Run the lower layer into another Squibb funnel and wash twice more with ether. Treat the upper layer twice with a mixture of 25 per cent sodium hydroxide solution and water (about 30 cc. of 25 per cent NaOH in all) and then finally with water. Wash the alkaline and water extracts in turn with the same ether used in washing the first aqueous extract. Combine the ether extracts and washings, carefully distil the ether on the water bath, and weigh the residue as neutral oils.

Combine the alkaline and water extracts obtained above, acidify with sulfuric acid (1 + 4), and steam-distil until no more phenols come over (test with ferric chloride solution). Saturate the distillate with salt and extract three times with ether. Carefully evaporate the ether and weigh the residue as phenols. (In case of large quantities of phenols they may be extracted from the ether above with 25 per cent sodium hydroxide and then liberated with sulfuric acid (1 + 4) and measured. The weight of phenols should be considered as 1.05 times the volume. For accurate work corrections must be made for the water in the phenols and for the phenols in the acidified solution of sodium sulfate.)

Extract the residue in the distilling flask with ether, evaporate the ether, and weigh the residue as fatty or resin acids (or a mixture of fatty and resin acids). Multiply this weight by 0.97 to obtain the weight of fatty and resin anhydrides.

The rosin acids in the mixed acids may be determined by Wolff's¹ method.

Sodium or Potassium Oxide.—Use the same method as for sodium or potassium oxide in soap, p. 561.

The principal difficulty in the method for the neutral oils is that of evaporating all the ether without losing some of the neutral oil. This is especially true if they contain any considerable proportion of the lower boiling fractions. In practice it is often found advisable to remove the last traces of ether by blowing a current of air on the oil after removing it from the steam bath. An experienced operator can get quite accurate results on most samples with this method, however, in spite of its difficulty. The same difficulty in regard to evaporating ether occurs in the method for determining phenols. In addition the phenols have a tendency to hold water so that the phenolic residue remaining after the distillation of the ether may contain as much as 10 per cent of water. Usually the two errors counterbalance each other to a considerable extent.

OTHER METHODS FOR EMULSIFYING DISINFECTANTS

The following methods recommended by Chapin,² differ somewhat from those just described.

¹ *J. Ind. Eng. Chem.*, **14**, 1161 (1927).

² U. S. Dept. Agr. Bur. Animal Industry Bull. **107** (1908).

Water.—Weigh 50 grams of the sample into a 100 cc. fractionating flask with a moderately high side tube, beyond which the neck should continue for not more than 1 inch. Connect the flask with a small water-cooled condenser and carefully heat with a smoky flame until oils come over freely and carry no water with them, but do not continue the distillation unnecessarily. Receive the distillate in a graduated 25 cc. cylinder, allow to stand for some time to separate completely, and then read the volume of water. A sample extremely high in rosin may bump and froth over. In such a case a large flask should be used, and the sample diluted with about an equal quantity of water-free mineral or coal tar oil. If the separation of the distillate into layers is imperfect, add a small measured quantity of strong sodium chloride solution, nearly fill the cylinder with benzol, shake, and allow to rest for some time. Read the volume of the aqueous layer and subtract from it the volume of salt solution used. Consider each cubic centimeter of corrected volume to represent 1 gram of water, and calculate its percentage.

Phenols.—Weigh 50 grams of dip into a 500 cc. round-bottomed flask, add 20 cc. of sulfuric acid (1 + 3), and distil off the phenols with steam. If a rapid current of steam is passed into it, the flask will require no heating, but may with advantage be packed in cotton or felt. Obviously the apparatus must be so set up and the distillation so conducted that particles of rosin may not be mechanically carried over by the current of steam. Toward the end of the distillation melt out any naphthalene in the condenser by shutting off the water for a few minutes, or if naphthalene is separated earlier in sufficient quantity to threaten stoppage of the condenser tube, interrupt the distillation and run hot water through the condenser. Receive the distillate in a liter flask marked approximately for each 100 cc. capacity. Join the flask to the condenser by a cork through which passes a small glass tube connected to a small U-tube containing a little dilute sodium hydroxide. The latter acts as a trap to prevent any loss of the distilled phenols. Continue the distillation until 1 or 2 cc. collected in a test tube gives no reaction with any appropriate reagent for phenols, such as ferric chloride. A volume of 800 cc. should prove ample in nearly all cases.

Prepare a supply of benzol by shaking a good grade of benzol with dilute sulfuric acid, then with dilute sodium hydroxide two or three times, and then passing through a dry filter. A small wash bottle containing some of this benzol will be found very useful for rinsing the necks of separatory funnels, etc. Measure 150 cc. of this purified benzol and place it conveniently at hand. Add the contents of the U-tube and 5 cc. of sulfuric acid (1 + 1) to the distillate, shake the latter, pour into a separatory funnel of 1500 cc. capacity, and rinse the flask with successive portions of the 150 cc. of benzol. When all is in the funnel, add 25 grams of clean sodium chloride for each 100 cc. of distillate, shake the funnel well for 5 minutes, and allow to rest for 30 minutes. Then run off the aqueous layer slowly and completely, and allow the funnel to stand until there is no further separation. Transfer the benzol solution of phenols and hydrocarbons to a 500 cc. Erlenmeyer flask, pour the aqueous portion back into the separatory funnel, and extract twice more in the same way, using 100 cc. of benzol each time. The funnel should always be gently handled after the aqueous portion has been drawn off to prevent any impurities from the sodium chloride which have deposited upon its sides from becoming mixed with the benzol solution. Unite the 3 benzol extracts in the Erlenmeyer flask, add 15 cc. of pure sodium hydroxide solution (1 + 2), and subject the contents of the

flask to a rotatory motion for some time in order that the phenols may be taken up by the sodium hydroxide as completely as possible. Add a few grains of sand to the flask, immerse in a water bath, connect to a condenser, and distil off all but 40-50 cc. of the benzol. Next, with the aid of a wash bottle containing water and provided with a fine jet, carefully wash the contents of the flask into a 150 cc separatory funnel, using only a small portion of water at a time. With proper manipulation the flask should be completely washed when the volume of aqueous portion in the separatory funnel amounts to not more than 50 cc. Next slowly introduce with gentle rotation of the funnel, 10 cc. of sulfuric acid (100 cc. of concentrated sulfuric acid plus 120 cc. of water). Interrupt the addition of acid whenever the funnel becomes unpleasantly warm to the hands. Now add 2 or 3 drops of methyl

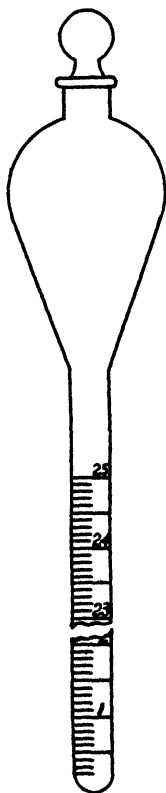


FIG. 10.—Phenol Measuring Tube.

orange, and if on mixing the contents of the funnel the lower layer does not acquire a pink color continue the addition of acid until acidity is assured. Then add sufficient benzol to make the two layers in the funnel approximately equal in volume. Thoroughly shake the funnel and allow to stand for 2 hours with loosened stopper.

Then slowly and completely run out the aqueous layer, making sure that on longer standing no more will drain down from the sides of the funnel. At this point the benzol solution of phenols is ready to be transferred to the measuring tube.

The measuring tube, Fig. 10, consists of a glass-stoppered pear-shaped bulb of about 100 cc. capacity, joined at its tapering end to a tube about 1 foot long and of a capacity of 25-30 cc. This tube is accurately graduated to contain 25 cc. at 20° C. in divisions of 0.1 cc.

The apparatus must be thoroughly cleaned with soap powder and hot water, and dried, best spontaneously, though alcohol and ether may be used if pure. Perfect cleanliness is essential to insure a properly shaped meniscus. Place between 15 and 16 cc. of sodium hydroxide solution (1 + 3) in the tube by means of a pipet, without allowing the solution to come in contact with the interior of the bulb or upper part of the tube. After a few moments add about 1 cc. of benzol and after waiting a little note the height to the top of the now almost flat meniscus. Next transfer the benzol solution of phenols from the separatory funnel to the tube, taking care to avoid mixing with the soda. Wash out the separatory funnel with a little benzol, transfer the washings to the tube, and again note the position of the meniscus. The position of the meniscus may often be obtained more accurately at this point. Stopper the tube, shake vigorously for 3 minutes, and set aside for at least 3 hours. An occasional rapid rotation of the tube between the palms of the hands will insure a more complete separation of the layers. Each cubic centimeter of increase in volume of the sodium hydroxide solution may be taken to represent 1 gram of phenols. Take all readings of the tube at the top of the meniscus and at a temperature as near 20° C. as practicable.

Rosin Acids.—These acids may be determined either gravimetrically or volumetrically. Cool the contents of the flask from which phenols have been steam-distilled and pour the aqueous portion into a separatory funnel, with as little rosin as possible, and extract with ether. Draw off and discard the aqueous portion. Dissolve the residue in the flask with ether, transfer the solution to the funnel, add 50-60 cc. of water, and shake the funnel well. The presence of insoluble carbonaceous matter will usually cause a persistent emulsion at the junction of the two layers, which may, in fact, entirely fill the lower part of the funnel. Draw off the lower layer, including any emulsion, into a 300 cc. Erlenmeyer flask and again shake the ether layer with successive portions of water, until the carbonaceous matter is wholly removed and separation takes place in the funnel quickly and cleanly. Receive all of these wash waters in the flask containing the first separated emulsion and heat this on a steam bath until the ether is expelled. Then bring the contents more or less completely upon a wet filter and wash with hot water. At this point the methods diverge.

Gravimetric method.—Drain well both flask and filter after a brief washing of the insoluble carbonaceous residue with hot water. Then wash both, first with a little absolute alcohol to remove water, then thoroughly with ether until all rosin is dissolved and the filtrate comes through colorless. Unite the ethereal solution of hydrocarbons and rosin and shake with about 40 cc. of 15 per cent sodium hydroxide solution. On separation there will be three layers. The lowest one will usually contain little rosin soap and consequently hold but a small amount of hydrocarbons. It is best run off and washed separately with ether. One washing will usually free it completely from hydrocarbons. After the first layer has been thus

removed, add about 50 cc. of water to the funnel and shake well. Run off the lower layer of rosin soap and follow with 5–10 cc. of water without shaking, the funnel being given only a gentle rotatory motion. Wash the remaining ether solution of hydrocarbons twice with 20–25 cc. of about 4 per cent sodium hydroxide solution, following each washing by a little water, as before described. Keep these two washings with sodium hydroxide apart and do not add to the main solution of rosin soap.

Wash the main solution of rosin soap in a separatory funnel with successive portions of ether and follow through each time by 5 cc. of water, as at first, until the ether is left nearly colorless. Shake the ether extracts through in their order with the two washings of dilute sodium hydroxide already used, and a third if needed, following each with a few cubic centimeters of water.

Unite all the aqueous extracts in a porcelain dish or casserole, which should be not more than half filled by them, and evaporate on a steam bath until the ether is dissipated and the volume reduced to a convenient quantity. Transfer the contents of the dish to a separatory funnel with the aid of a spatula and hot water; add sulfuric acid to decompose all rosin soap, and after complete cooling extract the rosin acids with ether and wash with water until free from sulfuric acid. Bring the ethereal solution into a weighed Erlenmeyer flask containing a few grains of sand, distil off the ether, heat the flask in an oven at 110° C. until the absence of frothing on rotation of the flask shows elimination of water, then cool and weigh.

Volumetric method.—In the volumetric method proceed exactly as in the gravimetric method to the point where carbonaceous matter is brought upon the filter and washed with hot water. In this case continue the washing until the wash water comes through entirely free from acid reaction. Meanwhile bring the main ethereal solution into a flask and distil off the ether. Set the filter funnel in the neck of this flask and wash the carbonaceous matter until freed from rosin with hot alcohol previously rendered neutral to phenolphthalein. Bring the alcoholic solution of rosin into a volumetric flask and take an aliquot part, usually one-fourth, for titration with 0.5 *N* sodium hydroxide solution. This titration is conveniently carried out in a 200 cc. Erlenmeyer flask in a volume of 100–125 cc., the portion taken being diluted with neutralized alcohol to that amount.

Owing to the very dark color of the liquid an external indicator is necessary. For this purpose alkali blue is best adapted. Add a few drops of a strong alcoholic stock solution to 25 or 30 cc. of alcohol, and carefully neutralize with 0.1 *N* sodium hydroxide solution. Use sufficient alkali blue to produce a deep color, almost a cherry with no trace of violet, when neutralized. This dilute indicator should be freshly prepared. During the titration of the rosin acids, have at hand cleaned and dried a supply of small test tubes 8–10 mm. in diameter and 60–80 mm. long. When a test of the titration is to be made, pour about 0.5 cc. of the prepared indicator into one of these test tubes and add a drop of the liquid under titration. If a violet color appears, the solution still contains free rosin acid and more of the 0.5 *N* sodium hydroxide must be added and the solution again tested with a fresh tube of indicator. If the indicator does not show a violet color upon the addition of one drop of the liquid under titration, continue to add the latter drop by drop until 0.5 cc. has been added, which is a quantity approximately equal in volume to the indicator originally in the tube. The continued absence of a violet color after

the addition of this amount indicates that the solution is either neutral or alkaline. The end of the titration is reached when a greenish or violet tint just fails to appear. A fresh tube of indicator must be used for each test. It is best to proceed by first running in 12–15 cc. of 0.5 *N* sodium hydroxide at once, then test, and if necessary continue the addition, a cubic centimeter at a time, until the indicator shows alkalinity; run back with 0.5 *N* hydrochloric acid using perhaps 0.4 cc. at a time until acidity is shown, and then work carefully with 0.5 *N* sodium hydroxide to exact neutrality. Consider 1 cc. of 0.5 *N* sodium hydroxide equivalent to 0.162 gram of rosin acids. Phenolphthalein may also be used as an indicator in a similar way by preparing an alcoholic solution of quite a deep rose tint. The end point of the titration will then be reached when the indicator, used in the same way as alkali blue, is no longer bleached by the addition of the liquid under titration. The color change is not so marked as in the case of alkali blue, and consequently the end point is not so sharp, though almost equally good results may be obtained with a little care and practice. All alcoholic solutions should be kept from contact with air as far as possible to prevent absorption of carbon dioxide.

Soda and Pyridine Bases.—In the determination of soda and pyridine bases a measured volume of standard sulfuric acid, known to be in excess, is added to change these bases to the sulfates and to liberate the free rosin acids, which are then separated. Then the excess sulfuric acid is titrated with alkali to a methyl orange end point, giving sodium sulfate and pyridine sulfate in solution. The same solution is then titrated to a phenolphthalein end point. The difference between the two titrations is the equivalent of the pyridine bases present and is calculated to pyridine (C_5H_5N). The difference between the total alkali titration and the original standard sulfuric acid added is the equivalent of the soda in the sample and is calculated to sodium oxide (Na_2O).

Coal Tar Neutral Oils.—The coal tar neutral oils are calculated by difference. This value is to be considered as only approximate since the errors in the determinations of all the other components will affect it.

The determination of phenols by the method of Chapin has been criticised on the ground that each cubic centimeter increase in volume of the alkaline solution does not always represent a gram of phenols. Edwards and Freak¹ showed that, using various phenols, the errors could vary from 7 to 17.5 per cent. However, in practice the method has proved fairly satisfactory, and consistent results can be obtained by its use.

High-Boiling Phenols.—In using either of the two methods described for determining phenols in emulsifying coal tar disinfectants it should be realized that, since the phenols are distilled with steam, high-boiling phenols will not be included in the determination. Edwards and Freak have stated that the phenols distilling above 250° are volatile in steam only with difficulty and are not correctly determined by these methods.

¹ *J. Soc. Chem. Ind.*, **39**, 326 T (1920).

Ordinary coal tar creosotes contain comparatively little of the high-boiling phenols and there has been no practical difficulty due to their presence. However, blast furnace tars and tars which are produced by the low-temperature carbonization of coal are known to contain considerable quantities of high-boiling phenols. These are particularly valuable because their use will often markedly increase the bactericidal efficacy of a disinfectant. Taylor¹ suggested a method for the determination of phenols that would include the higher-boiling bodies, as follows.

Weigh 50 grams of disinfectant into a 250 cc. Pyrex side-neck distilling flask, add 25 grams of sodium bicarbonate and 0.5 gram of magnesium carbonate, and wash down the sides of the flask with 50 cc. of a high-boiling refined petroleum distillate that has been previously washed with alkali. Connect the flask with a Liebig condenser and collect the distillate in a Weiss, type 2, measuring tube. Continue the distillation over a free flame at a slow rate until the distillate attains a deep yellow color. Transfer the water that collects in the tube to a separatory funnel, salt out any phenols present, dissolve them in kerosene, and add this solution to the distillate in the measuring tube. Wash with 10 cc. of 10 per cent sulfuric acid, discard the acid wash, and note the volume in the tube at 25° C. Remove the phenolic bodies with successive 80 and 60 cc. portions of 10 per cent sodium hydroxide solution and after thorough draining note the final volume in the tube at the same temperature. Multiply the diminution of volume in cc. by 1.03 to obtain the weight in grams of phenol present

Mineral Oil.—Mineral oil is sometimes found in emulsified disinfectants as an adulterant. It is of no value as a disinfectant, and a method for its determination is therefore desirable. There is no method which is entirely satisfactory, but it is possible to make a fair estimate from the percentage of unsulfonated residue from the oil as follows:

Sulfonate 5 cc. of the neutral oil separated from the disinfectant as described on p. 600 with 38 *N* sulfuric acid by the method described for lubricating oils on p. 566, and determine the volume of unsulfonated residue, if any. Determine the refractive index (N_D) at 20° by means of an Abbé refractometer as a check on the type of oil.

True coal tar distillates may contain a small quantity of unsulfonated residue. Church and Weiss² found as high as 6.2 per cent of unsulfonated residue from one of the distillates of a vertical retort tar. This must be taken into account in considering whether the oil is adulterated. The refractive index for the D line at 20° C. is about 1.44-1.45 for kerosene and

¹ *J. Assoc. Official Agr. Chem.*, **11**, 222 (1928).

² *J. Ind. Eng. Chem.*, **6**, 396 (1914).

somewhat higher for the higher boiling petroleum oils. The refractive index for the residue from a true creosote oil is still higher.

Phenol.—Phenol (C_6H_5OH) in emulsified coal tar disinfectants may be determined by the method of Chapin given on p. 585 without any previous treatment. It has been found that the rosin soap and neutral oils do not interfere.

NAPHTHALENE

Naphthalene is a common constituent of louse powders and is also used alone as a protection against clothes moths. It is sometimes dissolved in oils.

Samples Composed Entirely of Naphthalene.—If the sample consists of naphthalene unmixed with other substances the only determination necessary to be made is the melting point, which is determined as described in the chapter on physical methods, section (g). Pure naphthalene melts at 79° – 80° C.

Naphthalene in Mixtures

APPARATUS

(a) *Watch-glasses.*—Three watch-glasses, diameter 10 cm., whose edges have been ground to a plane.

(b) *Electric hot plate*—An ordinary laboratory hot plate, wired for low, medium and high heats.

REAGENTS

Calcium oxide.—Recently ignited and cooled.

DETERMINATION

Weigh a quantity of the sample that will contain 0.25–0.3 gram of naphthalene and transfer to a watch-glass, described under (a). Cover with a second glass of the same kind that has been previously weighed and heat on the electric hot plate. Use a temperature sufficient to volatilize the naphthalene in about 30 minutes, keeping the upper glass cool with a blast of air projected downward against it. (The medium heat of the hot plate will usually suffice.) When the naphthalene has volatilized and collected on the upper glass, remove the glasses from the hot plate, but do not separate them, and allow them to cool under air blast. Remove the upper glass, place it over a second weighed glass to prevent loss of the naphthalene and weigh. Clean the upper watch-glass, return it to the first glass and again heat to insure the complete sublimation and recovery of the naphthalene. Weigh any additional naphthalene obtained. From the combined weights of the sublimes and the quantity of sample taken, calculate the percentage of naphthalene.

If the sample contains sufficient moisture to cause an error by depositing with the naphthalene, mix the sample with about an equal quantity of the freshly ignited quicklime before sublimation.

In lieu of the apparatus described above, any efficient sublimation apparatus may be used. A satisfactory one is described by Fuller.¹

Naphthalene in Oils

It will be necessary only occasionally for the insecticide chemist to determine naphthalene in oils. Hamor and Padgett² have described a method for this determination. The naphthalene is volatilized by drawing a current of air through the oil contained in a test tube immersed in a hot water bath and connected to a reflux condenser. The naphthalene is absorbed in saturated picric acid solution contained in a series of bottles connected to the upper end of the condenser. The quantity of naphthalene picrate is determined by titration with standard sodium hydroxide, from which the percentage of naphthalene is calculated.

PARADICHLOROBENZENE

Paradichlorobenzene is extensively used as a soil fumigant to kill peach tree borers. It is usually encountered unmixed with other substances, and it is only necessary to judge its purity by its melting point, which is determined as described in the chapter on physical methods, section (g). The melting point of pure paradichlorobenzene is 53.1° C.

Paradichlorobenzene can be separated from powders in which it is occasionally found by the sublimation method described under naphthalene. It has a characteristic aromatic odor which is a valuable aid in its detection.

The percentage composition of mixtures consisting only of paradichlorobenzene and naphthalene can be determined by comparing the melting point of the mixture with that of known mixtures of these two substances.

¹ *Chemist Analyst*, No. 20, 6 (1910).

² *The Chemical Examination of Crude Petroleum, Petroleum Products and Natural Gas*, 1920, p. 236.

CHAPTER XV

MISCELLANEOUS INSECTICIDES

Most of the products covered in this chapter contain several ingredients and are of such diverse nature that in most cases only general directions can be given. Therefore to the analyst is left the task of applying the principles of analytical chemistry to the problem presented by the particular sample with which he has to deal.

ROACH POWDERS

Roach powders usually contain as the active ingredient sodium fluoride, borax, boric acid, pyrethrum, or mixtures of these materials. They may consist entirely of these ingredients, but they generally contain an inert filler such as starch, flour, cacao shells, talc or diatomaceous earth. The material most commonly used without admixture, except for the impurities incidental to its manufacture, is sodium fluoride.

All samples of roach powders should be examined by an experienced micro-analyst for the detection and possible estimation of organic constituents for which no chemical methods are available.

Boric Oxide.—*Qualitative Test.*—Place from 1 to 5 grams of the sample in a small flask, add 30–40 cc. of methyl alcohol, acidify with sulfuric acid, and close the flask with a stopper through which passes a tube with a small aperture. Heat the flask sufficiently to boil the alcohol gently and ignite the vapors at the point of emergence. A green color in the flame indicates the presence of boron. This test can often be satisfactorily carried out in an open dish, although in this case the green color due to minute quantities of boron is not so easily seen and hence the test is not so delicate as that made with the flask and tube.

Quantitative Determination

DETERMINATION

1. *In Boric Acid and Borax.*—(Applicable only in the absence of organic matter, fluorides, and salts of polybasic acids like phosphates, which are not titrated to the same degree when methyl orange and phenolphthalein are used as indicators.)

REAGENTS

- (a) 0.2 *N* sulfuric acid.—Standardize by precipitation as barium sulfate.
- (b) Standard alkali.—Prepare an approximately 0.2 *N* alkali solution and standardize against (a).
- (c) Neutral mannitol.
- (d) Neutral glycerol.

Digest 2 grams of the sample with 100–150 cc. of warm water in a 200 cc. volumetric flask for 15 or 20 minutes, shaking frequently. Cool to room temperature,

make to volume, and filter through a dry filter. Exactly titrate a 50 cc. aliquot of this solution with 0.2 *N* acid, using methyl orange as indicator. Boil to expel carbon dioxide, cool, and titrate with alkali until the color just changes to yellow. (At this stage all the boric acid will be in the free state.) Add about 10 grams of neutral mannitol and a few drops of phenolphthalein indicator, note the buret reading, and again titrate the solution with the standard sodium hydroxide until a pink color develops. Add a little more mannitol and if the pink color disappears continue the addition of the standard alkali until a pink color reappears. Repeat the alternate addition of mannitol and standard alkali until a permanent end point is reached. (A volume of neutral glycerol equal to one-half the volume of the solution to be titrated may be substituted for the mannitol.)

From this titration calculate the percentage of boric oxide on the basis that 1 cc. of normal alkali is equivalent to 0.03482 gram of B_2O_3 . If the results are desired in terms of boric acid or borax, substitute the following factors:

$$\begin{aligned} 1 \text{ cc. of } N \text{ alkali} &= 0.06184 \text{ gram of } H_3BO_3. \\ &= 0.05032 \text{ gram of } Na_2B_4O_7. \\ &= 0.09536 \text{ gram of } Na_2B_4O_7 \cdot 10H_2O. \end{aligned}$$

2. *In the Presence of Fluorine Compounds.*—(Applicable to mixtures containing both borax and sodium fluoride, in the absence of phosphates.)

REAGENTS

Calcium acetate solution—Dissolve 100 grams of calcium acetate in water and dilute to 1 liter.

The other reagents are described in the previous method.

DETERMINATION

Transfer a 100 cc. aliquot of the filtrate, prepared as described in the preceding method, to a 200 cc. volumetric flask, slightly acidify with acetic acid, and precipitate the fluorine with calcium acetate solution. Make to volume, shake thoroughly and allow to stand a sufficient time for the calcium fluoride precipitate to settle. Do not attempt to filter. Draw off a 100 cc. aliquot of the clear solution with a pipet, transfer to a platinum dish, add an excess of lime or lime water, evaporate to dryness, and ignite to destroy acetates. Take up with hydrochloric acid; exactly neutralize with sodium hydroxide, using methyl orange as indicator; and proceed as described in the preceding method, beginning with "Boil to expel carbon dioxide * * * ."

3. *In the Presence of Organic Matter and Phosphates.*—(Adapted from *Methods of Analysis*, A. O. A. C., and *A Systematic Handbook of Chemical Analysis*, F. Sutton, 11th ed., 99.)

REAGENTS

Sodium hydroxide solution.—Dissolve 250 grams of sodium hydroxide in water and dilute to 1 liter.

The other reagents are described in the previous methods.

DETERMINATION

Dissolve 2 grams of the sample in water, make distinctly alkaline with sodium hydroxide solution, and evaporate to dryness in a platinum dish. Ignite the residue

until the organic matter is thoroughly charred, avoiding an intense red heat; cool; digest with about 50 cc. of hot water; and add hydrochloric acid drop by drop until the reaction is distinctly acid to methyl orange. Filter into a 200 cc. volumetric flask and wash with a little hot water. Return the filter containing any unburned carbon to the platinum dish, make alkaline by wetting thoroughly with lime water, dry on a steam bath, and ignite to a white ash. Dissolve the ash in a few cubic centimeters of dilute hydrochloric acid (1 + 3) and add it to the liquid in the 100 cc. flask, rinsing the dish with a few cubic centimeters of water. To the combined solutions add 0.5 gram of calcium chloride and a few drops of phenolphthalein indicator, then 10 per cent sodium hydroxide solution until a permanent light pink color is produced, and finally dilute to the mark with lime water. Mix and filter through a dry filter. To 50 cc. of the filtrate add 0.2 *N* sulfuric acid until the pink color disappears, then add methyl orange indicator, and continue the addition of the acid until the yellow color is changed to pink. Continue the determination as described under determination of boric oxide in boric acid and borax beginning with "Boil to expel carbon dioxide * * *."

Other Constituents.—Sodium fluoride should be determined by one of the methods described in the chapter on fluorine compounds. Pyrethrum powder and cacao shells cannot be determined in such mixtures quantitatively by chemical means, but a fairly accurate estimation can be made by an experienced micro-analyst. The best method for starch is the diastase method.¹ Ash and acid-insoluble ash should be determined by the methods described under Pyrethrum. If the sample contains much borax it is best before ashing, to leach the sample with water, then ash the residue, add the leachings to the ash, evaporate, and ignite at a dull red heat.

ROACH PASTES

These preparations usually consist of yellow phosphorus mixed with starch, sugar, and water. The only determination ordinarily made is that of the phosphorus. Owing to the tendency of this constituent to settle to the bottom, it is extremely important that the sample be thoroughly mixed immediately before analysis. The sample should be oxidized with nitric and sulfuric acids, and the phosphoric acid should be determined by the official gravimetric method given under "Fertilizers."¹ The percentage of phosphorus is then calculated from the results of this determination.

This method gives the total phosphorus, both free and combined, but the result of the determination is usually considered to be free phosphorus since it is practically all uncombined.

¹ *Methods of Analysis, A. O. A. C.*

LOUSE POWDERS

Louse powders may contain sulfur, sodium fluoride, sodium silico-fluoride, derris powder, nicotine (tobacco powder), pyrethrum powder, naphthalene and phenols, mixed with inorganic fillers such as talc, lime, sand, Fullers' earth, or diatomaceous earth. However, it is not likely that all these ingredients will be found in the same preparation.

All samples of louse powders should be examined by an experienced micro-analyst for the detection and possible estimation of organic constituents for which no chemical methods are available.

Sulfur.—Determine by carbon disulfide extraction or oxidize directly as described under Elemental Sulfur. In the latter case make correction for any sulfur initially present as sulfate. If the sulfur obtained by extraction is contaminated with other matter, oxidize and determine the sulfur by precipitation as barium sulfate.

In some samples it is best to proceed directly by one of the oxidation methods without first extracting with carbon disulfide.

Nicotine.—This usually occurs in louse powders in the form of powdered tobacco, which can generally be detected by its odor or identification of tobacco tissues by the microscope. Determine quantitatively by the silico-tungstic acid method, described under "Tobacco."

Fluorine.—Make qualitative tests on the sample by the etching or hanging drop tests described in the chapter on Fluorine Compounds; if a positive test is obtained, prepare a water extract of the sample and determine the fluorine in the solution as described in that chapter.

Naphthalene.—Naphthalene may be detected by its characteristic odor. Determine it quantitatively by sublimation, as described in the chapter on Coal Tar Products.

Phenols.—Phenols in louse powders can usually be detected by their odor. For a quantitative determination proceed as follows:

Weigh 10–20 grams of the sample, transfer to the flask of a steam distillation apparatus, acidify with sulfuric acid, and steam distil into a Squibb separatory funnel until no more phenols come over in the distillate, as shown by a test with ferric chloride. Separate and determine the phenols from this distillate as described in the chapter on Coal Tar Products.

Pyrethrum.—Pyrethrum also has a characteristic odor by means of which its presence can usually be detected in louse powders; definite identification may be made by means of a microscope. At present there are no chemical methods for estimating its percentage in such mixtures, but an experienced micro-analyst can make a fairly accurate estimation of the quantity present.

Ash and acid-insoluble ash should be determined as described under Pyrethrum Powder.

ANT POISONS

Most ant poisons on the market are preparations containing a compound of arsenic, and occasionally antimony (tartar emetic), mixed with sugar, sirup or honey. The preparation recommended in U. S. Dept. Agr. Farmers Bull., 1101 for the control of the Argentine ant contains sodium arsenite, sugar sirup, honey, tartaric acid and sodium benzoate.

Arsenic and antimony, which are the active ingredients, are generally the only constituents determined in such preparations. The sample taken for analysis should be first oxidized with nitric and sulfuric acids to destroy the organic matter, and the nitric acid should be expelled by heating until the sulfuric acid evolves white fumes. After cooling and diluting with water, a second fuming is necessary to expel nitrosyl sulfuric acid. The arsenic can then be determined by the Gooch and Browning method or by one of the distillation methods previously described. If the sample contains both antimony and arsenic the latter should be removed by the hydrazine sulfate distillation method and the antimony recovered from the residue in the distillation flask by precipitation with hydrogen sulfide, after which the antimony sulfide may be dissolved in hydrochloric acid (1 + 1) and estimated by the Gooch and Browning method.

FLY POISONS

Porous paper is often impregnated with a water-soluble form of arsenic, usually sodium arsenite, and sold for killing flies.

For analysis small pieces should be cut from different parts of the sheet in order to get a uniform sample. These should then be oxidized and the arsenic determined in the same way as for the Ant Poisons.

Arsenical fly killing preparations are also sold in flat tin cans with wicks protruding from the top. The preparation usually consists of sodium arsenite, white arsenic, or metallic arsenic mixed with sugar. In use the can is kept filled with water, and the flies are poisoned by drinking the poisoned liquid absorbed by the wicks.

The contents of the cans should be analyzed by the methods recommended for Ant Poisons and Poison Papers.

PREPARATIONS FOR THE CONTROL OF BEDBUGS

A large number of the preparations sold for the control of bedbugs consist of solutions of phenols in a light mineral oil of the nature of gasoline or kerosene. They may also contain other constituents such as nitro-

benzene and carbon tetrachloride. All of these constituents are active against bedbugs and thus quantitative estimation is not always required.

The determinations usually made on such preparations are specific gravity, the distillation range, sulfonation residue and phenols. Nitrobenzene and carbon tetrachloride are less frequently determined. Nitrobenzene can usually be detected by its odor, and in doubtful cases the isonitrile test is very satisfactory for its identification. The percentage of nitrobenzene present can be determined, after extraction of phenols, by reducing with zinc dust and hydrochloric acid and then titrating with standard bromide-bromate solution. The carbon tetrachloride can usually be identified by its boiling point and refractive index in the fraction of the distillate coming over between 75° and 80° C. If carbolic acid (phenol) is present, it should be determined by the Chapin method, p. 585. This determination is necessary, because if more than 5 per cent is present the product must be labeled according to the provisions of the Federal caustic poison act.

FORMALDEHYDE SOLUTIONS

Formaldehyde solutions, which are largely used for household disinfection, find additional agricultural application for seed disinfection. For analysis of such preparations an aliquot of the sample is oxidized with hydrogen peroxide in the presence of a known quantity of standard alkali. The resulting formic acid is determined by a titration of the excess standard alkali with a standard acid, litmus or bromthymol blue being used as indicator.¹

¹ *Methods of Analysis, A. O. A. C.*

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